

INDUSTRIAL CATALYSIS

by

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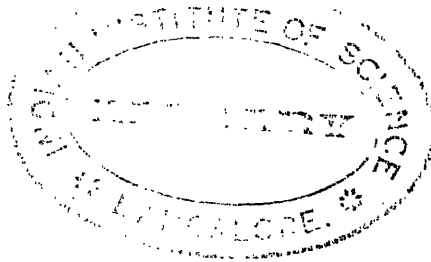


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PREFACE

THE last twenty-five years have witnessed the advance of the chemical industry to a leading position among the world's great industries. This is partly a consequence of the recent European war, since the resources then mobilised could only be dealt with upon a scientific basis. A slower evolution must, however, in any case have occurred and be still in operation, since in technology, as in pure science, each forward movement supplies a new resource—either of knowledge or material—to aid the next advance. Industries founded and developed upon a scientific basis, so long as they are maintained upon that basis, may therefore be expected to progress at an accelerating rate as continuously increasing resources are brought into use—an expectation many times realised within the last decades. For example, Clerk-Maxwell supplied an idea which, in the hands of others, notably Marconi, has led to the development of radio-telephony, with enormous present-day consequences and future potentialities, such as television and, perhaps, transmission of power by radiation. Engineering, one of the oldest industries reared upon a foundation of pure science, only prospers when the latest results achieved by the physicist are promptly utilised. The fixation of atmospheric nitrogen by various processes has deeply influenced the numerous industries (especially agriculture) employing Ammonia and nitrates.

This mutual influence, of discovery in one sphere and development based upon it in many others, has frequently been demonstrated, while Chemistry and Physics have been recognised as the fundamental sciences, Industry and all other sciences (including even Biology) being in greater or less degree derived.

"Catalysis" is a narrowly specialised region of Physics and Chemistry, but industrially, as the sequel will show, an extremely important one. In *Industrial Catalysis* the author has purposed first to record the discovery of the scientific facts that come within the scope of the title; secondly, to show how these facts have been utilised or applied; and, thirdly, to observe the general consequences following the discovery and application.

Incidentally, it may be remarked that *Industrial Catalysis* is an outcome of a lengthy period—about thirteen years—devoted to

chemical research, mainly catalytic. The author's indebtedness during this time to the compendious treatise of Sabatier and to the able and versatile work by Rideal and Taylor may be frankly acknowledged. The end which *Industrial Catalysis* has attempted to reach is a different one, and has already been intimated. To attain it, the author has not hesitated to use freely all the sources of information provided by other authors, but it is hoped that a considerable residue remains representing opinions or results based on experience.

To many friends, helpers and advisers, the author tenders sincere thanks.

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CHAPTER I

SURVEY OF CATALYSIS FROM THE TIME OF THE EARLIEST OBSERVED INSTANCES TO ITS PRESENT-DAY DEVELOPMENT

The Three Periods of Advance—(1) Pre-Berzelian; (2) Period of Scientific Research and Discovery; (3) Period of Industrial Application. Early Discoveries. Observations of Mrs. Fulhame, Kirchhoff, H. Davy, Erman, Thenard, E. Davy, Dobereiner, Dulong and Thenard, Henry, Phillips, Turner, Payer and Persoz, Liebig and Mitscherlich. The Views of Berzelius. Faraday's Researches and the Adsorption Theory. Clément and Désormes and Williamson and the Intermediate Compound Theory. The Chemical Reaction. Views of Bergmann and Berthollet. Investigations of Wilhelmy, Williamson and Berthelot and Pean de St. Gilles. Guldberg and Waage's Law. Extension of Guldberg and Waage's Law. Application of Thermodynamics to Physics and Chemistry. Function of the Catalyst. Researches by Hautefeuille and Lemoine. Industrial Development. Present Trend of Manufacturing Chemistry.

IN an historical study it is usually possible to distinguish periods of time corresponding with marked stages in the progress of thought or of achievement. These periods may be well defined, as when a great event, or a character of outstanding personality, changes within a few years the whole trend of thought or of action. More often, by a natural sequence of advances, the periods merge one into the next, allowing in point of time no sharp demarcation to be distinguished, and only in retrospect, over many years, is it possible to see that far-reaching changes have gradually become accomplished. Following this conventional line of treatment, we can see that our special subject, "Catalysis," may, up to its present-day development, be divided into three principal periods.

The first is a clearly-defined one, in which isolated observations were made and sometimes recorded, but no effort was made to systematise or explain them. This period began when, at a date lost in the past, sugar was first fermented to alcohol, and terminated when Berzelius critically examined, and classified under the term "Catalysis," all those diverse types of actions which the name denotes. He saw clearly from recorded facts that certain chemical reactions involve a distinct and rather curious principle—that a substance can cause a chemical change, and yet, apparently, not participate in it. The prestige of Berzelius' name, the publicity of

his celebrated "Lehrbuch" and "Jahresberichte," together with the distinctive term "Catalysis," attracted notice to the subject, and many new instances were soon recognised, and efforts—notably by Faraday and by Liebig—made to explain them.

This commences the second period—one of systematic research and discovery, whereby it eventually became apparent that, far from being an unusual phenomenon, Catalysis was a principle of remarkable universality. This view reached its culmination in the dictum of Ostwald, that "there is probably no type of chemical reaction which cannot be influenced catalytically, and there is no substance, element or compound, which cannot act as a Catalyser."

The second period, that of steady growth of scientific knowledge, merged gradually into the third, that of wide industrial application. Towards the end of the last century, when the number of known catalytic reactions had increased to hundreds, the economic possibilities of many of them commenced to be exploited, sometimes on a great scale. The manufacture of Ether from Alcohol, using Sulphuric acid as catalyst, and the oxidation of Sulphur dioxide to Sulphuric acid, using oxides of Nitrogen as Oxygen carriers, had long been in use. With the growth of Chemical Industry, and the increasing demand for Chemical products, processes of manufacture in which one of the components was not consumed, and in which bye-products were less likely to be formed, possessed evident economic advantages. The climax of this period was reached during the great European War, when, in the case of the Central Empires at least, external resources were cut off, and the enormous supplies of explosives and foodstuffs required were dependent upon new methods and a new organisation. Hence, between 1914 and 1919, we find the catalytic processes for Sulphuric acid, Ammonia (Haber process), Nitric acid (Oxidation of Ammonia), and hydrogenation of oils organised and carried out on a prodigious scale.

If the post-war years have shown a decline in these processes, it is already evident that from the point of view of catalytic processes as a whole this is only temporary. New industries of far-reaching significance are already springing into existence, as, for example, the synthesis of Methyl alcohol, the manufacture of synthetic petrols from water gas, and liquid fuels by hydrogenation of coal.

We will now consider the development of these three periods in greater detail.

First Period.—The experimental data accumulated up to the time of Berzelius comprised a number of diverse reactions, many of which are cited in his "Jahresberichte" for 1836. Among the reactions known at this date, all simple types, including fermenta-

tion, can be recognised, and the extreme bounds of the subject of catalysis were set by Berzelius when he said that "Catalytic force" was "common both to Organic and Inorganic Nature."

In the ancient and middle ages, the processes of fermentation of sugar to spirits of wine and of wine to Acetic acid were well known. The origin of these processes is too remote to trace, but alcohol seems not to have been isolated until the Alchemical era, and Acetic acid was not distinguished from the sharp-tasting constituents of fruit juices. The only example of inorganic catalysis known in ancient times was probably the conversion of Alcohol into Ether when heated with Sulphuric acid. The first exact description of this method was given by Valerius Cordus, a German physician of the sixteenth century, and published after his death, about 1552, by Conrad Gessner. The process, however, was in vogue long before the publication of Cordus' instructions.

The alchemical period which succeeded may be looked upon as one of fruitless search for a non-existent and impossible catalyst, the "Philosopher's Stone," which should transmute indefinite quantities of base materials to noble ones.

Knowledge of chemical reactions among the Alchemists, and even among many generations of chemists which followed, could only have been empirical. Not until the fundamental laws of chemical union, especially Conservation of Matter, were better understood would it be possible for any conception to be formed distinguishing between a catalytic and any other chemical reaction. Hence, until the ideas of Lavoisier, Cavendish, Priestley, Berthollet, Proust, Gay-Lussac, and Dalton had gained some measure of acceptance (1790 to 1810), there could be no realisation of any unusual feature in the fact that a body could induce a chemical reaction and yet remain unchanged.

The first reaction in which the catalytic principle was properly appreciated was discovered by Mrs. Fulhame ("An Essay on Combustion," London, 1794; Mellor, *J. Phys. Chem.*, 1903, 7, 557), who found that the oxidation of metals, the reduction of metallic oxides, and the combustion of Carbon monoxide all required the presence of small quantities of water, which was not altered in the reaction.

Kirchhoff (*Schweigger's Journal*, 1812, 4, 108) hydrolysed starch to sugars by heating with dilute acids, and proved that the acid was unchanged.

In a communication to the Royal Society, January 1817, Sir Humphry Davy stated that a piece of Platinum wire, or foil, when warmed and plunged into a mixture of Oxygen or air with various combustible gases (Hydrogen, Carbon monoxide, Coal gas, Ethylene, Cyanogen, Hydrocyanic acid, Alcohol or Ether vapour, etc.), became

incandescent, and caused combination of the mixed gases, often with explosion. Davy stated "a temperature much below ignition only was necessary for producing the curious phenomenon, and the wire was repeatedly taken out and cooled in the atmosphere till it ceased to be visibly red, and yet, when admitted again, it instantly became red hot" (*Phil. Trans.*, 1817, 107, 77). Erman observed in the following year that the Platinum wire required to be warmed only to 50° C. to bring about this interaction.

Thenard (*Ann. Chim. Phys.*, 1818, 9, 96, 314) showed that Hydrogen peroxide was stable in acid solution, but decomposed to water and oxygen in presence of alkalies. Many other substances, such as Silver, Platinum, Gold, and Fibrin, were also found to facilitate this decomposition, but at different rates.

Edmund Davy (*Phil. Trans.*, 1820, 100, 108) showed that finely-divided Platinum ("Platinum-black"), soaked in spirits of wine and exposed to air, effected oxidation of the spirit to Acetic acid. Spontaneous inflammation sometimes supervened.

Dobereiner (*Schweigger's Journal*, 1822, 34, 91; 1823, 38, 321) prepared spongy Platinum by igniting the double chloride of Platinum and Ammonium. He confirmed Davy's observation of two years earlier, showing that this spongy Platinum, when gently warmed, determined oxidation of Alcohol, in contact with air, sometimes accompanied by explosion. He also found that cold Platinum sponge induced combination between Hydrogen and Oxygen, and upon this observation based the "Hydrogen lamp," a well-known curiosity of earlier days.

Dulong and Thenard (*Ann. Chim. Phys.*, 1823, ii, 23, 440; 24, 380) extended Dobereiner's observation by investigating the conditions under which other substances besides Platinum effected this union. They found at a suitable temperature that many substances (Silver, Gold, and even Glass) aided the union of Hydrogen and Oxygen.

Henry (*Phil. Mag.*, 1825, 65, 269) carried out a series of remarkable experiments on selective combustion of various gases in presence of Platinum, and discovered incidentally the powerful inhibiting effect that certain substances (for example, Carbon monoxide, Sulphuretted hydrogen, Carbon disulphide, etc.) exert towards this catalyst. He considered it strange that Platinum, which caused such energetic action between Hydrogen or Carbon monoxide, and Oxygen should have so much less influence when compounds of Carbon and Hydrogen (Ethylene or Methane) were used instead. This selectivity of the catalyst he hoped to employ in analysing and separating gaseous mixtures. The results, expressed almost in Henry's own words, were as follows: When the action of the Platinum sponge was moderate, only the Hydrogen and Carbon monoxide were consumed, and the Ethylene at most was but partially

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acted upon. Thus, when combustible gases, mixed with each other, with Hydrogen, and with Oxygen, were exposed to Platinum sponge, the several gases were not acted upon with equal facility. Carbon monoxide was most disposed to unite with Oxygen, then Ethylene, and lastly Methane. By due regulation of the proportion of Hydrogen, it was possible to burn the whole of the Carbon monoxide without attacking the Ethylene or Methane. Henry further showed that when a mixture of equal volumes of Hydrogen, Carbon monoxide, and Oxygen was exposed to the action of Platinum sponge at an advanced temperature, 80 per cent. of the Oxygen united with the Carbon monoxide, and only 20 per cent. with the Hydrogen. This observation showed plainly the retarding influence of Carbon monoxide towards the union of Hydrogen and Oxygen in contact with Platinum.

Turner in 1824 (*Edinburgh Phil. Journ.*, 1824, 11, 99, 311) had shown that Platinum promoted the union of Hydrogen with Chlorine, and in 1831 the use of the same metal was patented for the atmospheric oxidation of Sulphur dioxide (Phillips, E.P. 6069 of 1831).

The conversion of starch into sugars by acids, and in various physiological processes, recognised long previously, was proved by Payer and Persoz, to be due to the action of an "unorganised ferment." These investigators, in 1833, isolated Diastase from the extract of barley malt and proved that it was able to effect this conversion quite independently of any living organism (*Ann. Chim. Phys.*, 1833, ii, 53, 73). Diastase was the first enzyme to be recognised, and its action on starch was particularly remarked by Berzelius as entirely comparable with that of the inorganic substances which effected the same reaction. A few years later, Liebig isolated another enzyme, Emulsin, from bitter Almonds, and showed that the characteristic action of Emulsin was independent of presence of living tissue.

Mitscherlich's classical investigation of the action of Sulphuric acid on Ethyl alcohol (*Pogg. Ann.*, 1834, 31, 273) established that relatively small quantities of acid sufficed to convert large quantities of Alcohol into Ether, and that the gradual slackening of its action was due to the effect of a bye-reaction which gradually brought about its decomposition. Commenting upon this work of Mitscherlich, Berzelius states that the conversion of Alcohol into Ether is clearly not dependent simply on the affinity of Sulphuric acid for water, since it is possible by suitable adjustment of conditions to add Alcohol to Sulphuric acid and obtain a regular evolution of water and Ether. The Sulphuric acid in this reaction is therefore analogous to the Diastase in the conversion of starch into sugar, and the alkali in the decomposition of Hydrogen peroxide. Berzelius' conclusion

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may be stated in his own words: "It is then shown that several simple and compound bodies, soluble and insoluble, have the property of exercising on other bodies an action very different from chemical affinity. . . ." "The body effecting these changes does so not by taking part in them; it remains unaltered, and therefore acts by means of an internal force, whose nature is unknown to us. . . ." "This new force, hitherto unknown, is common to organic and inorganic nature."

To the founder of the "Dualistic Theory," which regarded the forces of chemical affinity as electrical in origin, it was natural that electrochemical analogies should suggest themselves. Berzelius continues: "I do not believe that this force is independent of the electrochemical affinities of matter; I believe, on the contrary, that it is a new manifestation of the same, but, since we cannot see their connection and interdependence, it will be more convenient to designate the force by a new name. I will therefore call it the 'Catalytic Force,' and I will call 'Catalysis' the decomposition of bodies by this force, in the same way that we call by the name 'Analysis' the decomposition of bodies by Chemical Affinity." The antithesis between Catalysis (*κατά*, down; and *λύω*, I loose) and Analysis (*ἀνά* and *λύω*), expressed so pointedly, shows how the term "Catalysis" was derived, and indicates that Berzelius was not, as has been suggested, indebted to Libavius for its invention. As used by the latter author ("Alchemia Recognita," Lib. II., Vol. I, Chaps. XXXIX, XL; Frankfurt, 1611) its significance appears never to have been understood.

Berzelius defined a catalyst as follows: "A substance that, by its presence, and not by its affinity, has the power to rouse latent affinities, so that compound substances undergo interaction, and a greater electrochemical neutralisation occurs."

Second Period. The Advance of Scientific Knowledge of Catalysis.—Even before the publication in the "Jahresberichte" of Berzelius' memoirs, a great English contemporary had taken the first step in the scientific study of catalysis. The "Law of Definite Electrolytic Action" overshadowed the minor discoveries made by Faraday in the course of the experimental researches which led to that important generalisation.

Using a Hydrogen-Oxygen voltameter, Faraday was surprised to find a deficiency of gases frequently resulting from the electrolytic decomposition of water. Sometimes even a disappearance of gas was observed after it had actually been collected and measured. These discrepancies were traced to the catalytic influence of the Platinum electrodes, which caused a recombination of the Hydrogen and Oxygen. The interesting observations were also made that the positive Platinum electrode was more active in this respect than

the negative, and was also able to cause Hydrogen and Nitrous oxide slowly to interact. To this point, Faraday's observations constituted merely a confirmation of Dobereiner's and Davy's. His further experiments, simple but convincing, brought to light several fundamental facts of catalysis, and the explanation he advanced has developed almost without modification into the modern adsorption theory.

In the first place, Faraday proved that a perfectly clean metallic surface was essential, or the Platinum was comparatively inert. Such a surface could be obtained electrolytically by making the Platinum a positive electrode, also by scouring with acids, alkalies, charcoal, etc. The state of the metal, whether spongy and porous or compact and burnished, merely altered its degree of activity. This activity, however, tended gradually to diminish and eventually to disappear. The period of activity depended upon the purity of the gases used, and the presence of some impurities, even in small quantities, quickly and completely suppressed it. For example, a little Carbon monoxide, or Carbon disulphide vapour, in the Hydrogen and Oxygen mixture prevented the action of the Platinum. The metal had not lost its activity, however, since on transferring to pure gases it caused them to combine. A trace of Sulphuretted hydrogen, or Hydrochloric acid, on the other hand, so altered the metallic surface that its catalytic activity was permanently lost. From these experiments Faraday argued that the catalytic action of Platinum was a surface phenomenon. He conceived the solid surface to exert a powerful attractive force on the particles of gas surrounding it, whereby the latter were brought into such close proximity both with the surface and with one another as would exist if they were in the liquid state. Interaction between molecules, brought together in this way, then follows, if circumstances are favourable, as, for example, in the case of Hydrogen and Oxygen, or (to a less degree) Nitrous oxide and Hydrogen.

Faraday also attributed the anticatalytic effect of a soiled surface, or one of the inhibiting agents mentioned, to the true cause, namely, a superior attraction of the surface for these substances, preventing effective contact between the surface and the Hydrogen and Oxygen. Faraday's work was published in the *Philosophical Transactions* for 1834 (114, 55) and in "Experimental Researches on Electricity," London, 1849. Several generations passed before Faraday's ideas of surface action and adsorption gained their due recognition. J. J. Thomson then developed on their basis a consistent theory of Catalysis.

The possibility of interaction between two substances being effected through the intermediation of a third, which participated in a series of cyclic changes, had already been observed by Clément

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and Désormes, using oxides of Nitrogen to oxidise Sulphurous to Sulphuric acid (*Ann. Chim.*, 1806, 59, 329). The continuous production of Sulphuric acid was supposed to be due to the alternate formation of "Chamber crystals" from Sulphurous acid and Nitrogen peroxide, followed by their decomposition into Sulphuric acid and Nitric oxide, the cycle then being completed by atmospheric oxidation of the Nitric oxide. The total effect of this series of changes consisted in oxidation of Sulphurous acid by air, *via* Nitric oxide and "Chamber crystals." This was the first attempt to explain catalytic reactions by the formation of intermediate compounds with the catalyst. Nearly fifty years later, Williamson suggested a similar mechanism for explaining the continuous formation of Ether from Alcohol and Sulphuric acid, and the conception gradually expanded into the modern "Chemical Theory" of catalysis.

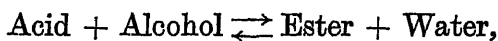
In this section of our study of the development of catalysis it is not our purpose to enumerate the examples of catalytic reactions steadily accumulating. We must rather follow the trend of ideas relating to the mechanism of chemical change, and see then how the functions of a catalyst in these reactions became recognised.

Bergmann, 1775, supposed a chemical change proceeded in one direction only, and to completion. The affinities of substance, however, were admitted to vary according to certain circumstances, such as temperature, and whether the reaction were carried out in a "wet" or a "dry" way.

Berthollet, in 1801, suggested that the quantities and relative proportions of reacting substances as well as their affinities were involved. This view was first established quantitatively by Wilhelm (Pogg. Ann., 1850, 81, 413, 499), who proved conclusively that in the inversion of cane-sugar there was a definite rate of reaction, and that this rate was directly proportional to the concentration of the cane-sugar solution at each instant.

The conception of speed of chemical reaction was quickly followed by the recognition that chemical reactions are frequently reversible, thus Williamson, in 1851, as a result of his classical experiments on etherification, concluded that a balanced interchange between the reactants occurred.

Berthelot and Pean de St. Gilles, in 1862, found that the esterification of an acid with an alcohol was a simple reversible chemical reaction,



and proved that the initial rate of esterification of an acid was directly proportional to the product of the concentrations of acid and alcohol present.

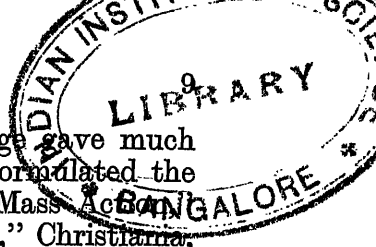
SURVEY OF CATALYSIS

The two Norwegian chemists Guldberg and Waage gave much greater precision to these experimental results, and formulated the first quantitative law. According to the "Law of Mass Action," developed in their "*Études sur les Affinités Chimique*," Christiania, 1867, the tendency for chemical reaction to occur between substances is directly proportional to the product of their "Active Masses." By active mass was implied the number of molecules or equivalents of a substance per unit of volume, synonymous with the more modern term "Concentration." The extent of a chemical change was therefore equal to the product of the active masses of the reacting substances, and a constant, which Guldberg and Waage proposed to call the "Coefficient of Affinity," measuring numerically the "chemical force" tending to bring about the reaction. Guldberg and Waage's work remained in obscurity for some years, and their law was developed independently by Jellet (1873) and by Van 't Hoff (1877). Van 't Hoff pointed out that the constant in the mass action equation was really a speed constant, and could be used definitely to measure the amount of chemical change in gram-molecules per unit of time. This proposal, so much more definite than the vague conception of affinity, gained immediate acceptance.

The experimental justification of the Law of Mass Action resulted from the work of many investigators. Wilhelmy's research on the rate of inversion of cane-sugar and that of Berthelot and Pean de St. Gilles on the esterification of acids by alcohols have already been mentioned. Harcourt and Esson (1864), investigating the rate of interaction of Hydrogen peroxide and Hydriodic acid, provided further data. Subsequent to its formulation, many researches by a large number of different workers, among whom may be mentioned especially Van 't Hoff, Bodenstein, Arrhenius, and Ostwald, completely established the universal validity of the Mass Law.

The recognition of reversibility of chemical reactions led at once to the conception of chemical equilibrium, that is, the point at which two opposing reactions are taking place at the same speeds. The Law of Mass Action established the relations existing between varying concentrations of reactants and the speed of chemical reaction, and therefore enabled the position of equilibrium to be defined.

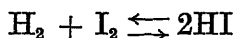
The effects of temperature and pressure on chemical change were first stated in the form of general laws by Le Chatelier (1884) and by Braun (1887-8). On the basis of the laws of Thermodynamics, and of Guldberg and Waage's Law, these effects have been expressed quantitatively in mathematical form, and the equations so derived tested by direct experiment. Prominent among those who have so profitably applied thermodynamic reasoning to the study of chemical



and physical change may be mentioned Van 't Hoff, Horstmann, Gibbs, and Nernst. Their results, in so far as they concern our subject, will be dealt with in a later chapter.

It must now be emphasised that the generalisations we have reached were established for all chemical reactions, whether catalytic or not. We must now consider how the function of the catalyst came to be distinguished.

It was shown experimentally by Hautefeuille (*C.R.*, 1867, 64, 608), and more completely by Lemoine (*Ann. Chim. Phys.*, 1877, (5), 12, 145) that in the reversible system



for all temperatures, the same point of equilibrium was reached from whichever direction it was approached. It was further shown that the presence of a catalyst (*e.g.*, Platinum), while it much increased the rate at which equilibrium was attained, did not alter its position. Thus Lemoine found that when Hydriodic acid at 2 atmospheres pressure was heated to 350° C., slow decomposition occurred, and at the end of 300 hours 18.6 per cent. had changed to Hydrogen and Iodine. In the presence of Platinum sponge, and at ordinary pressure, 19 per cent. decomposition was attained almost at once. The Platinum therefore hastened decomposition, but did not alter the amount when equilibrium had been reached. Shortly after, the same conclusion was deduced from thermodynamic considerations, and stated generally, as follows: A catalyst which (*ex hypothesi*) contributes no energy to a chemical system cannot change the position of equilibrium, it can only alter (*i.e.*, retard or accelerate) the rate at which it is reached. Ostwald, in 1888, carried this view of the catalytic function to the length of maintaining that a catalyst cannot initiate a chemical change, it can only accelerate or retard a reaction that is already, to some extent, occurring. This view has been strongly contested, and it would certainly appear that many reactions, which cannot be proved to take place at all in the absence of a catalyst, can easily be effected when a catalyst is added. If the two views are considered more carefully, it will appear that the difference between them is merely a hypothetical one, since a reaction taking place infinitely slowly is for practical purposes not taking place at all.

In the foregoing account it has been attempted to present the origin and growth of those ideas which it is the purpose of our later chapters to expand in detail. Simultaneously with the development which we have been reviewing, and especially during the last forty years, the number of known catalytic reactions has increased enormously. Many are of general application and can therefore be classified as "Hydrogenations," "Reductions," "Dehydrations,"

etc. From this vast number of reactions, many have been chosen on account of their economy, for industrial application, to the manufacture of chemical or other products, in some cases on a gigantic scale.

Third Period. The Development of Industrial Catalysis.—Within recent years progress in all branches of industry has been impressively rapid. This may be attributed to two main causes. First, to the increased resources made available by the application of scientific methods to production, organisation, and control. Secondly, it must be regarded as a natural response to the demands of an age characterised by world-wide advance in the standard of life. Luxuries of an earlier age become necessities to a later, when the means of supply are made cheap and abundant. Hence the rapid growth of all existing fields of industry and the inception of new, providing substitutes to augment the older source of supply no longer adequate. Artificial silk, synthetic resins, and chemically hardened edible fats have already become the bases of great industries.

The enormous development of industry generally has only been made possible by the corresponding development of chemical industry, upon which many—perhaps all—others are in greater or less degree dependent. Germany and America have led in this latest advance, during which the world output of Metals, Acids, Alkalies, Dyes, Drugs, Soap, Rubber, Perfumes, etc., must have multiplied many times since the commencement of the present century. Industries less fundamentally chemical, such as Textiles, Flour-milling, Agriculture, and Mining, have likewise found vastly increased resources in the advance of scientific industry and in the application of scientific research and control, directed to reorganisation of old methods and initiation of new. As a direct consequence of many factors, whereas forty years ago the number of individual chemical substances manufactured in bulk was comparatively few, the requirements of the modern world can only be satisfied by thousands.

It is our present purpose to see how catalytic methods have assisted the development of chemical industry. Their potentialities were foreseen by Ostwald (address: see *Z. Elektrochem.*, 1901, 1, 995): "The scientific knowledge and control of catalytic phenomena must lead to immeasurable results in a technical direction. The last great triumph of German technical chemistry, the synthesis of Indigo, which reverses the economic relationships of nations, contains as an essential factor a new catalytic reaction. The oxidation of Naphthalene by Sulphuric acid can only be carried out satisfactorily in presence of Mercury. That the Sulphuric acid itself is obtained by catalytic agency alike in the old as in the new

process, I need only recall. If one considers that the acceleration of reaction by catalytic means occurs without expenditure of energy or material, and is in this sense gratis, it is evident that the systematic use of catalysts may lead to the most far-reaching advances in technology."

If the fermentation industries are excepted, the oldest catalytic large-scale processes are the manufacture of Sulphuric acid by the lead chamber process and the manufacture of Ether from Alcohol. The formation of Sulphuric acid from burning brimstone and moist air had been known for centuries, but the first attempt at commercial exploitation was about 1740, when Ward, at Richmond, in Surrey, burnt charges of Sulphur and saltpetre in glass bell jars, and collected the products in water between each charge. Roebuck, in 1746, substituted lead vessels for glass. Large-scale production commenced in the early years of the nineteenth century, when Hill used pyrites as the source of Sulphur dioxide, and when, shortly after, the Gay-Lussac tower was added to the plant. By 1883, the annual production of Sulphuric acid by this process had increased to 50,000 tons in England alone.

About this time, the rival method, also catalytic, was developing into a manufacturing process. As far back as 1831 it was discovered by Peregrine Phillips, a vinegar manufacturer of Bristol, that heated Platinum effected the union of Sulphur dioxide and Oxygen (E.P. 6069 of 1831). The commercial application of this process was found, however, to involve great difficulties, which were not surmounted until many years later, when it was shown that purity of the interacting gases was of vital importance in order that the catalyst might retain its activity. In spite of these difficulties, which defeated the application of the process to the manufacture of Sulphuric acid from crude gases, Squire and Messel, using as starting materials the gaseous heat decomposition products of oil of vitriol, had commenced the manufacture of Sulphur trioxide in their works at Silvertown (E.P. 3278 of 1875). It was not until 1898 that the problems connected with the manufacture of "contact" Sulphuric acid were completely solved by the investigations of Knietsch and his collaborators. Their results have been outlined in a lecture by Knietsch to the German Chemical Society (*Ber.*, 1901, 34, 4069; *J. Soc. Chem. Ind.*, 1902, 21, 172). Since 1900 the contact process of manufacture has increased to an enormous scale, though it has not completely displaced the older method, which in certain circumstances is more advantageous. The impressive rate of advance of the Sulphuric acid industry is sufficiently emphasised by the remark that the average annual world production since 1916 has exceeded 10,000,000 tons.

Catalytic processes for manufacture of Hydrogen and Hydro-

generated products, Chlorine and Chlorinated products, various "heavy chemicals," and innumerable other substances have developed into very important industries. Purification of coal gas, vulcanisation of rubber, polymerisation, hydration, dehydration, and partial combustion of organic substances, all involve catalytic reactions which are now applied, in some cases, on a great scale. The catalytic oxidation of Ammonia developed and organised in Germany during the war maintained the whole supply of Nitro-explosives for the Central Empires.

Of comparatively recent growth are the catalytic gas reactions involving high pressures. From theoretical considerations it had long been recognised that the union of Nitrogen and Hydrogen was only prevented by the weak "affinities" of the two gases for one another. In other words, a high "chemical friction" impeded their interaction. A catalyst should therefore be possible which would overcome this tardiness of Nitrogen and Hydrogen to combine. It was further recognised that pressure would assist their union, and the compositions of equilibrium mixtures of Nitrogen, Hydrogen, and Ammonia for varying temperatures and pressures of the three constituents were deduced. The pioneer work of Haber and Le Rossignol (*Z. Elektrochem.*, 1913, 19, 53; *J. Soc. Chem. Ind.*, 1914, 33, 49) translated these theoretical speculations into technical practice. In 1913, the Badische Anilin- und Soda-Fabrik produced some 20,000 tons of synthetic Ammonium sulphate, and by 1918 single units were making 20 tons per day of anhydrous Ammonia. The total German production of anhydrous Ammonia for 1918 must have exceeded 250,000 tons.

During the war, and in the years immediately following, the same company was exploring the possibility of obtaining Methyl alcohol from Carbon monoxide and Hydrogen, under pressure. In 1923, it was stated that technical production of synthetic Methyl alcohol had reached 10 tons per day, and that the output was rapidly increasing. Georges Patart, in France, who has published details for carrying out this reaction, contests the German claim for priority of discovery, but up to 1925 large-scale production of Methyl alcohol by this method was in the hands of the Badische Company alone.

Very modern researches by Franz Fischer and his collaborators, and by Bergius, point the direction towards which industry is now moving, and the time may be confidently anticipated when those countries which are rich in coal deposits, but lack mineral oils, will be synthesising substitutes for the latter from products derived from the former. Water gas under high pressure, and in contact with a catalyst, produces a volatile liquid mixture ("Synthol") capable of substituting petrol in internal-combustion engines. Hydro-

genation under pressure is stated to convert coal into a mixture containing a high percentage of volatile liquids. The importance of the Methyl alcohol and Synthol syntheses, from the point of view of the economic use of coal, is evident, and gasification, recovery of coal-tar bye-products, followed by use of the coke in one of these reactions, may well constitute the next great forward move in modern industry.

CHAPTER II

THE PHENOMENA OF CATALYSIS

Definitions. Properties of Catalysts: (a) They survive a Reaction without Change or Loss; (b) Small Quantities transform Indefinite Quantities of Reactants. (c) They alter the Rate of Chemical Reaction, but do not disturb a Chemical Equilibrium. Apparent Exception to these Laws. Negative Catalysis; (a) Preservation of Hydrogen Peroxide; (b) Protection of Metals from Oxidation or Corrosion; (c) Preservation of Sodium Sulphite; (d) Antiknock Compounds. Autocatalysis: (a) Positive; (b) Negative. Anticatalysis. Promotion or Activation. Pulsating Catalysis. The Specific Properties of Catalysts. Scope of the Subject of Catalysis. Classification of Catalysts: (a) Carriers; (b) Adsorbent Contact Agents; (c) Electrolytic Contact Agents; (d) Water; (e) Dissolved Electrolytes; (f) Enzymes; (g) Inorganic Colloids. Other Types of Catalysts not included in Noyes and Sammet's Classification: (a) "Accelerators"; (b) Effects of Catalysts in an Electrolytic Bath; (c) Effects of Solvents. Manufacture of (a) Dimethyl Sulphate, (b) Sulphuryl Chloride; (c) Menshutkin's Researches.

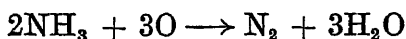
The General Properties of Catalysts

WHEN interaction in a chemical system is in any way modified by the presence of a foreign substance which undergoes no permanent change in quantity or composition, the reaction is a "Catalytic" one, the foreign substance which effects the modification is termed the "Catalyst," and the phenomenon is designated "Catalysis."

Berzelius' definition of catalysis, which may be accepted at the present time, has already been quoted. According to Ostwald ("Lehrbuch," 1896), a catalyst is a substance which alters the speed of a chemical reaction without being changed itself in the process. Bodenstein (*Chem. Zeit.*, 1902, 26, 1075) adopts this definition, and expresses it thus:—"A substance which accelerates or retards a reaction by its presence, but which cannot initiate a reaction, or disturb an equilibrium." Falk ("Catalytic Action," 1922) proposed a definition which is independent of any theoretical concept of catalysis, as follows: "A catalytic reaction is one in which the quantity and the chemical composition of one of the initial substances are identical with those of one of the products of reaction."

Whichever definition we accept, it is clear that the distinguishing feature of a catalyst is that it survives a chemical reaction without loss or change of composition. This may be taken as strictly true, since although in some cases a catalyst may be consumed, this is due, not to the main reaction, but to a slower secondary or by-reaction which gradually uses it up. For instance, in the production

of Ethylene from Alcohol, in presence of Sulphuric acid, a subsidiary reaction slowly reduces the latter to Sulphur dioxide. But for this, a small amount of Sulphuric acid would dehydrate indefinite quantities of Alcohol to Ethylene. If Phosphoric acid is used instead, reduction does not take place, and the "life" of the catalyst is increased indefinitely. Although the chemical characters of a catalyst are not altered in a reaction, the physical shape or properties may be considerably changed. Thus, surfaces of metallic Copper used to effect the reaction



or of Platinum gauze used for the oxidation of Ammonia to Nitric acid become roughened and pitted, as microscopic examination shows (Imison and Russell, *J. Soc. Chem. Ind.*, 1922, 41, 37T). This preliminary "wearing" of a catalytic surface frequently much increases its catalytic power, as, for example, in the case of Copper oxide, which becomes much more active, and effects its characteristic actions at a considerably lower temperature, after some hours' use.

The changes produced in Copper and Copper oxide by this activation have been examined by Taylor (*Trans. Am. Electrochem. Soc.*, 1919, 36, 154). Ordinary oxidised Copper wire of commerce is not rapidly reduced by Hydrogen at temperatures below 300° C. If, however, reduced Copper, formed at 300° C., be reoxidised at the lowest possible temperature, the resulting oxide can be reduced much more easily, and by repetition an oxide can finally be obtained which can be reduced in Hydrogen at 100° C.

This greater reactivity of metal or oxide for oxidation or reduction, respectively, is accompanied by greater catalytic powers: metals and oxides prepared at low temperatures being much more energetic catalysts in all reactions. Nickel shows the same characteristics. Copper wire activated by this treatment shows the same pitted and roughened surface that Platinum wire assumes after activation in the Ammonia oxidation reaction. A period of induction—generally short—during which the catalytic surface is becoming accommodated to its function is characteristic of most contact catalysts.

Since a catalyst survives a reaction without loss or change, it follows that a small proportion of a catalyst is capable of transforming indefinite quantities of reacting substances. This corollary was recognised by the earliest workers, and soon came to be recognised as one of the simplest criteria of a catalytic change. In practical use, the quantity of reactants changed by a certain amount of catalyst is not, of course, unlimited. The limit is usually set by (a) Bye-reactions involving the catalyst, or other means whereby the catalyst slowly disappears, such as vaporisation. (b) Presence

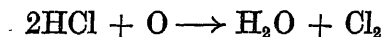
or accumulation of anticatalysts or poisons. The catalyst must then be either renewed or re-activated.

An exceedingly minute amount of catalyst is frequently sufficient to exert a very considerable influence. For example, Titov (*Z. Phys. Chem.*, 1903, 45, 641) found that in a Copper sulphate solution of 10^{-13} normal strength, the rate of oxidation of Sodium sulphite was perceptibly greater than in pure water.

Since a catalyst survives a chemical reaction without loss or chemical change, and, moreover, can induce change in an indefinite quantity of reactants, it follows that its energy contribution to a reacting chemical system is zero. Now since all chemical reactions involve an energy change, it follows that in a reversible system in equilibrium the addition of a catalyst can cause no change in that equilibrium. Thus, if it were otherwise, and addition of a catalyst enabled the equilibrium of a chemical system to be shifted in any direction, it would be possible either to create energy or to destroy it, by alternately adding a catalyst to the system and withdrawing it. A reversible chemical system will therefore arrive at the same position of equilibrium whether a catalyst is present or not, and the only effect produced by the catalyst will be to alter the rate of chemical reaction, and therefore the time taken to reach equilibrium. Also, since the equilibrium position in a reversible reaction is the same whether a catalyst is present or not, the speeds of both forward and reverse reactions must be influenced equally by the presence of a catalyst.

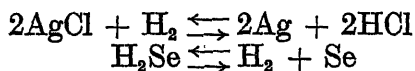
Many apparent exceptions to these laws have been described. Further investigation has shown, however, that these discrepancies admit of simple explanations quite consistent with the generalisations we have stated. The following reasons for apparent exceptions are common.

1. Insufficient time has been allowed for the system to attain true equilibrium. Thus, Clarens (*Bull. Soc. chim.*, 1922, 31, 299) stated that the reaction

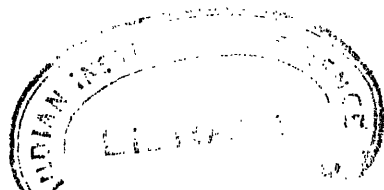


and its reverse (the "Deacon" chlorine process) were influenced by Copper salts to different degrees. Durand (*Bull. Soc. chim.*, 1922, 31, 759), however, considered that the gases had not been allowed time to reach a true equilibrium.

Equilibrium, especially in the absence of a catalyst, may in some reactions require months to be established, and, near the equilibrium position, the rate of change of composition of a reacting system may be very slow. Equilibria in the systems :



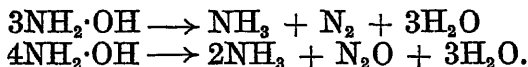
and



are, it is stated, different according to the direction of approach. It is probable that in these reactions equilibrium is very difficult to attain, the reactions becoming so slow as to be almost imperceptible as equilibrium is approached. When, therefore, the equilibrium is approached from opposite directions, there will be a considerable difference in composition at the points where further change becomes inappreciable.

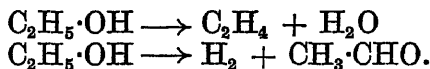
2. The active mass of one of the reactants may be altered by combination with the catalyst. In such cases, displacement of the equilibrium will naturally follow, and its position will depend upon the amount of catalyst present. Thus, Jones and Lapworth (*J.C.S.*, 1911, 99, 1427) found that in the hydrolysis of Ethyl acetate with Hydrochloric acid the equilibrium position depended upon the amount of acid used, and varied in such a way that they inferred the formation of a compound $\text{HCl} \cdot 2\text{H}_2\text{O}$, this altering the active mass of the water. More recently, Kendall has shown that esters frequently form compounds with mineral acids (*J. Am. C.S.*, 1916, 38, 1712).

3. A system may undergo several distinct reactions simultaneously. If addition of a catalyst favours one of these reactions more than the others, it will alter the proportions of the various products. For example, Hydroxylamine decomposes in two ways:—



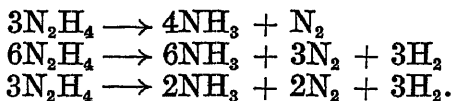
In hot aqueous solution, the former reaction preponderates, so that the products are Ammonia, Nitrogen, and water, with a little Nitrous oxide. When, however, Platinum-black is added, the speed of the second reaction is relatively much increased, and the main products are Nitrous oxide, Ammonia, and water, with but little Nitrogen (Tanatar, *Z. Phys. Chem.*, 1902, 49, 475).

Sabatier and Mailhe (*Ann. Chim. Phys.*, 1910, VIII, 20, 341) showed that Alcohol can decompose in two ways, according to the catalyst employed:—



With Thoria as catalyst, the first reaction takes place almost exclusively; other oxides, but more especially certain metals (best Copper), induce the second reaction to the apparent exclusion of the first, while most catalysts augment both reactions simultaneously.

Hydrazine undergoes decomposition in three ways:—



The first reaction is the main one with Hydrazine sulphate. Free Hydrazine decomposes mainly in accordance with the second, while the presence of alkali favours the third (Tanatar, *Z. Phys. Chem.*, 1902, 40, 475; 41, 37).

Addition of a catalyst can therefore in certain circumstances alter the composition of a product of reaction. It nevertheless remains true that for each individual reaction the only effect of a catalyst is to alter the speed, and not to affect the equilibrium.

These generalisations, that a catalyst cannot disturb an equilibrium in a reversible system, and must therefore influence both forward and reverse actions equally, have now been verified experimentally in many instances, and the only apparent exceptions are capable of simple explanation, as in the cases mentioned.

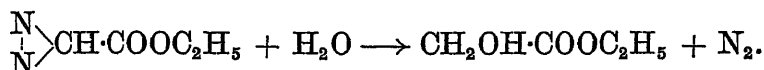
Ostwald's definition of catalysis implies that a catalyst cannot initiate a reaction, but can only alter the speed of one which is already, to some degree, happening, and this view has been both strenuously maintained and opposed. In propounding this view, Ostwald admitted that substances which easily react at a high temperature (*e.g.*, Hydrogen and Oxygen) can often be kept in contact indefinitely at a lower temperature without, apparently, any combination occurring. Nevertheless, since the rate of chemical change varies smoothly with the temperature, he claimed that some reaction, however little, must be postulated even at the lower temperature, and it is this action which it is the function of a catalyst to augment. Ostwald compared the action of a catalyst with that of a lubricant, which, by reducing friction, causes the speed of a machine to increase. Opponents of Ostwald's view, who hold that a catalyst can initiate a reaction, suggest that the analogy should be carried further and include the case of a machine actually stopped by friction and started by the application of oil. It is apparent that the two divergent views become reconciled if, on Ostwald's side, it is allowed that a catalyst may increase a reaction velocity from one infinitely small to one of finite value.

From consideration of Ostwald's ideas, one of the most valuable properties of catalysts can be inferred, that a catalyst can be employed to effect a reaction instead of a high temperature. In other words, since a catalyst increases the speed of reaction at all temperatures, a reaction which normally requires a high temperature can proceed at a much lower one if a suitable catalyst is present. In a manufacturing process this effect of lowering the reaction temperature increases the yield of the desired product in two ways: (a) Less decomposition occurs the lower the temperature, (b) a direct union of two reactants almost always occurs with evolution of heat. At lower temperatures the equilibrium of such a system will therefore be moved in the direction of greater percentage combination.

*

Influence of the Amount, or Concentration, of a Catalyst on the Rate of Reaction

In homogeneous systems the reaction velocity is directly proportional to the concentration of the catalyst, unless some influence comes into play which alters its active mass. This follows at once from theoretical considerations (Kinetic theory, and Law of Mass Action) and has been verified experimentally in a number of instances. Thus, the concentration of Hydrogen ions can be determined by the rate at which they catalyse certain reactions. For example, Curtius in 1883 showed that Diazo acetic ester is slowly decomposed by water :—



This reaction is powerfully catalysed by Hydrogen ions and furnishes a sensitive quantitative measure of their concentration, as shown by Fraenkel (*Z. Phys. Chem.*, 1907, 60, 202).

| Acid. | Concentration of Acid. Gr.-mols. per litre. | Concentration of Hydrogen-ions (C_H). | Monomolecular velocity constant (K) at 250. | Ratio. $\frac{K}{C_H}$. |
|---------------------|--|---|---|-----------------------------|
| Nitric . . . | { 0.00182 0.000909 0.000909 | 0.00182 0.000909 0.000909 | 0.0703 0.0346 0.0356 | 38.7 38.0 39.2 |
| Picric . . . | { 0.000364 0.000364 | 0.000364 0.000364 | 0.0140 0.0140 | 38.3 38.3 |
| meta-Nitrobenzoic . | 0.00990 | 0.00168 | 0.0632 | 37.7 |
| Fumaric . . . | 0.00364 | 0.00146 | 0.0571 | 39.1 |
| Succinic . . . | 0.00909 | 0.000724 | 0.0285 | 38.5 |
| Acetic . . . | 0.0182 | 0.000563 | 0.0218 | 38.7 |

The reaction was followed by reading in a gas burette the Nitrogen evolved from the reaction mixture, which was vigorously stirred to prevent supersaturation.

The same reaction has been employed to measure the suppression of ionisation of a weak acid brought about by addition of a strongly dissociated salt of that acid, and Walker has determined the Hydrogen-ion concentration of amphoteric electrolytes, *e.g.* Glycine, $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$, in the same way (see also Bredig and Spitalsky, *Z. anorg. Chem.*, 1907, 54, 265, and Bredig and Walton, *Z. Phys. Chem.*, 1904, 47, 185).

The decomposition of Diazo acetic ester is a particularly convenient reaction for investigation on account of the ease with which the reaction is followed and the simplicity of the catalytic process involved, which is due exclusively to the Hydrogen ions and only

inappreciably to the undissociated acid molecule. Other reactions (e.g., hydrolysis with acids) are usually catalysed both by the ions and by the undissociated acid molecules, and to different degrees, so that the proportionality between catalyst concentration and reaction velocity is obscured unless the acid is used at such dilutions that it is completely ionised.

In heterogeneous systems, the relation between the quantity of catalyst and the rate of reaction cannot be defined, since too many indeterminate factors are involved, such as the state of subdivision of the catalyst, the area of effective surface exposed, and the rate of diffusion of reactants through the resultants, to the catalytic surface.

When gases or vapour are passed over a contact agent, the period of contact of the reactants with the catalyst largely determines the amount of reaction, if other factors are maintained steady. This is generally expressed as a "Space Velocity" (S.V.) constant, which represents the number of volumes of gas (reduced to normal temperature) passed per unit of time through unit volume of the catalyst. Generally, for maximum efficiency, the rate of flow and the quantity of catalyst must be so adjusted that the space velocity constant is a maximum, consistent with maximum conversion and attainment of equilibrium, since in this way not only is the rate of production as great as possible, but the risk of decomposition by prolonged contact with hot catalyst is minimised.

Negative Catalysis

A catalytic change we have defined as one whose speed is altered by the addition of a foreign substance, or catalyst. Most commonly the alteration of speed is an acceleration ("Positive Catalysis," or simply "Catalysis"), but many instances of retardation are known. Retardation of a chemical action by influence of a catalyst is referred to as "Negative Catalysis."

Water, in minute quantities at least, is necessary for most chemical reactions, and therefore functions as a catalyst. In rather larger quantities, however, it sometimes behaves as a negative catalyst. For example, Than (*Ann.*, 1864, 131, 121) found that small quantities of water much retarded the decomposition of Ammonia into Nitrogen and Hydrogen. In accordance with the principles we have laid down, it must also retard in an equal degree the reverse change—the synthesis of Ammonia from Nitrogen and Hydrogen under pressure, and this is known to be the case. Van der Stadt (*Z. Phys. Chem.*, 1893, 12, 329) found that water retarded the oxidation of Phosphorus in air. The rate of decomposition of Diazo esters in alcoholic acid solution is slower in presence of water, and it was found by Grignard that Magnesium would not easily

dissolve in Ether solutions of alkyl or aryl halides unless water was scrupulously excluded. For preparation of Grignard's reagent, the solvent (usually Ether) must be efficiently dried by refluxing with metallic Sodium, or by prolonged contact with Phosphoric anhydride.

Oxygen retards the union of Hydrogen and Chlorine, and Carbon disulphide retards combination of Hydrogen and Oxygen. The decomposition which Oxalic acid undergoes when treated with strong Sulphuric acid is much retarded by the presence of a little water. Small quantities of Alcohol stabilise Chloroform towards light and air.

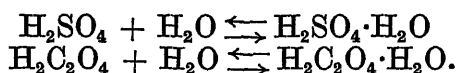
Luther supposed that negative catalysis was the result of partial destruction or inactivation of a positive catalyst already present. This view seems applicable to many reactions, especially those in liquid systems, where absence of a catalyst (which may be the solvent itself) can never be guaranteed. Titov (*Z. Phys. Chem.*, 1903, 45, 662) quotes in support of Luther's view the fact that the velocities of reactions are found to be inversely proportional to the concentration of negative catalyst present. This is a strong point, since we have already found that the reaction velocity is directly proportional to the concentration of a positive catalyst. Thus, Müller (*Z. Phys. Chem.*, 1902, 41, 483) found that the rate of hydrolytic decomposition of Bromosuccinic acid was directly proportional to the concentration of Bromosuccinic acid unchanged $\left(\frac{a-x}{v}\right)$ and inversely as the concentration of Hydrobromic acid formed $\left(\frac{x}{v}\right)$, which acts as a negative catalyst, that is

$$\frac{dx}{dt} = K \frac{a-x}{x}.$$

If one accepts the view that positive catalysis depends upon the formation of a labile intermediate compound between the catalyst and a reactant, then negative catalysis might be similarly explained as due to the formation of an intermediate compound which is not labile under the special energy conditions prevailing. Such a theory has been proposed by Taylor (*J. Phys. Chem.*, 1923, 27, 322) and Underwood (*Proc. Nat. Acad. Sci.*, 1925, 11, 78). According to Taylor, one of the reactants forms a molecular compound with the negative catalyst as an alternative to the normal reaction. Thus, Oxalic acid undergoes decomposition in presence of strong Sulphuric acid, and since Kendall has shown that organic acids tend easily to form Oxonium compounds with strong mineral acids, the reaction probably takes the following course:—



If water is present, however, both Oxalic acid and Sulphuric acid will form molecular compounds with the water,



and the rate of decomposition according to the first series of reactions will be diminished.

Underwood showed that stabilisers which are used to retard a decomposition, form molecular compounds with the substance preserved. For instance, Ether, Phenol, Resorcin, and Benzene all form molecular compounds with Chloroform, and can be used to stabilise it against the action of air and light. He has also shown that fugitive dyes can be protected against the action of light by treating the dyed fabric with a dilute solution of Phenol or Resorcin.

The inhibition of autoxidation processes has been systematically studied by Moureu and Dufraisse (*C.R.*, 1922, 174, 258; 175, 127; 1923, 176, 624, 797). The oxidation of aldehydes, such as Acrolein or Benzaldehyde, in air is strongly retarded by phenolic compounds, such as Hydroquinone, one molecule of which suppresses the oxidation of 40,000 molecules of Acrolein. The oxidation of Acetaldehyde, Chloral, Propionaldehyde, Anisic, Cinnamic, Hydrocinnamic, and Furfuryl aldehydes, Styrolene, Turpentine, linseed oil, nut oil, and butter is similarly influenced.

The colour changes associated with autoxidation, such as the darkening of Acrolein, as well as the common polymerisation of aldehydes, also are inhibited. Thus, Acrolein does not polymerise, and remains nearly colourless instead of rapidly blackening in presence of a small quantity of Hydroquinone or similar substance. Styrolene remains fluid, no longer forming Styrolene resin. Linseed oil can be exposed in thin layers to air without hardening, and fatty bodies do not become rancid. Thiourea, and phenols such as Hydroquinone, also protect silks against light, heat, and atmospheric action (Sisley and Seyewitz, *Bull. Soc. chim.*, 1922, 31, 672), synthetic and natural rubbers against autoxidation (*C.R.*, 1923, 177, 204; F.P. 509667 of 1919), and materials dyed with azo and eosin colours against fading (Moureu, Gillet, and Giot, *C.R.*, 1923, 176, 1402).

Christiansen has developed the idea of "chain reactions" to explain negative catalysis (*J. Phys. Chem.*, 1924, 28, 145. See also Weigert and Kellermann, *Z. Elektrochem.*, 1922, 28, 456). The molecule of a resultant, immediately after its formation in a reaction in which energy is developed, must contain a large excess of energy. Transference of some of this surplus to unchanged reactant molecules which it encounters leads to the activation and interaction of these, which in turn activate others, and so on. The negative catalyst is

supposed to act by absorbing the energy of the "hot" molecules, and interrupting or retarding the chain of events as described.

Instances of negative catalysis possessing a technical significance are the following:—

1. *The Preservation of Hydrogen Peroxide.* Hydrogen peroxide decomposes spontaneously into water and Oxygen. While this action is accelerated by the presence of many substances, others have a pronounced retarding action, e.g., Hydrofluosilicic acid, Sodium pyrophosphate, etc.

Heinrici (F.P. 356880 of 1906) proposed the use of various neutral organic compounds as preservatives, such as amides, imides, acetyl derivatives of aromatic bases, derivatives of urea, and especially Phenacetin.

Merck (Ger. P. 216263 of 1909) protected the use of Barbituric acid for this purpose. Uric acid also has a strong preservative action, but is not sufficiently soluble. Numerous other patents have appeared.

2. *The Protection of Metallic Surfaces from Oxidation or Corrosion.* This has usually been ascribed to the formation of a stable protective film. For example, there is reason to suppose that clean surfaces of Aluminium and Nickel oxidise rapidly in air to give a coherent, but very fine, film of oxide which prevents further action. Iron is stable when coated with the coherent Ferro-ferric oxide. Oxidation or corrosion of metals by solutions can often be retarded by addition to the solution of suitable negative catalysts. For example, Rohland (*Z. Elektrochem.*, 1909, 15, 865) showed that the presence of Chromic chloride solution retarded the rate of oxidation of Iron, and was effective even in presence of weak acids, such as Acetic, but not in presence of strong acids. Chromates and bichromates have a similar protective action.

Iron salts were found to protect Copper.

3. *Preservation of Sodium Sulphite Solutions.* Aqueous Sodium sulphite is readily oxidised by air to Sodium sulphate. Bigelow (*Z. Phys. Chem.*, 1898, 26, 493; 27, 585) showed that this oxidation was much slower in presence of such substances as Mannite, Benzaldehyde, or Benzyl alcohol. Mannite exerted an appreciable action at $\frac{1}{320000}$ Normal strength, while Benzaldehyde was even more effective, and a Sodium sulphite solution, which was 90 per cent. oxidised by air in 30 minutes in the absence of a negative catalyst, was only oxidised to the extent of 3 per cent. in a $\frac{1}{8000}$ Normal solution of Benzyl alcohol under the same circumstances. Young has shown that Nicotine and many other alkaloids, Ammonium salts, and Cyanides, similarly inhibit the oxidation of Sodium sulphite, and also of Stannous chloride (*J. Am. C.S.*, 1901, 23, 119, 450; 1902, 24, 297), and Lumière and Seyewitz have still further extended the

list, mentioning especially phenols (Hydroquinone, etc.) and bases (para-Amidophenol, Glycine, etc.) (*Bull. Soc. chim.*, 1922, 31, 672).

4. "Knock" Reducers, or "Antiknock" Compounds. Under certain circumstances the compressed gaseous mixture in the combustion chamber of an internal-combustion engine detonates violently instead of burning rapidly but smoothly. This produces a loud knock, as of metal against metal, and power is lost and risk of damage to the engine incurred. It has been shown by Midgley (*J. Ind. Eng. Chem.*, 1922, 14, 589, 849, 894; 1923, 15, 421) that detonation may be either suppressed or induced by adding suitable substances to the fuel mixture, which exert a negative or positive catalytic effect accordingly. Alcohol or Benzene, in gasoline or kerosene mixtures with air, much reduce the danger of detonation, so that a considerable proportion of benzole is added to the higher grades of petrols. Aromatic amines such as Aniline, Toluidine, Xylidine, etc., are very effective knock-reducers, while Diethyl selenide, $(C_2H_5)_2Se$, Diethyl telluride, $(C_2H_5)_2Te$, and especially Lead tetraethyl, $(C_2H_5)_4Pb$, exert a very powerful influence indeed. Midgley found that the presence of one molecule of Lead tetraethyl in over 200,000 molecules of combustible mixtures of kerosene with air exerted a marked effect in suppression of detonation.

✓Wendt and Grimm (*J. Ind. Eng. Chem.*, 1924, 16, 890) have described interesting experiments in support of their theory of the mechanism of antiknock action. It was supposed that the propagation of an explosion was facilitated by the electrons always formed by a flame being swiftly propelled into the bulk of the gaseous mixture, which absorbed their energy and became ionised and activated. The function of the antiknock agent was therefore twofold: (1) To attract the electrons. (2) To neutralise the hydrocarbon ions—both of which actions tended to reduce the normal rate of explosion. Their view was supported by (1) Lead tetraethyl, and other antiknock agents actually have a marked effect in causing gaseous ions to recombine. (2) Atoms containing unsaturated exterior electron rings should assume a negative charge with ease, and therefore act as antiknock agents, which is found to be the case.

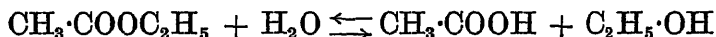
✓This theory was adversely criticised by Clark, Brugmann, and Thee (*J. Ind. Eng. Chem.*, 1925, 17, 1226). Knowledge of gaseous explosions has been collated by Clark and Thee (*J. Ind. Eng. Chem.*, 1925, 17, 1219).

Quite recently, the Badische Company has protected the use of Iron carbonyl as an antiknock agent.

Negative catalysis is to be distinguished from the inhibition of positive catalysis, which is brought about by anticatalysts or poisons, whereby the normal activity of a catalyst is reduced or stopped.

Autocatalysis

In certain cases, one of the products of a reaction may act as a catalyst of the reaction itself. Thus, esters are slowly hydrolysed by water :—

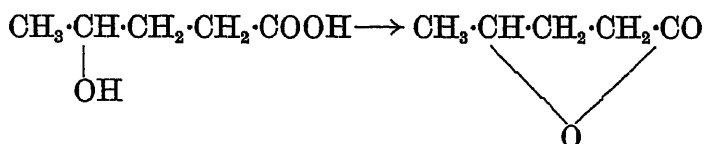


and this reaction is accelerated by the presence of Hydrogen ions. Now although organic acids are usually weak, they are nevertheless ionised to some extent, so that the acidic product of ester hydrolysis will catalyse further hydrolysis, and the reaction will proceed at a gradually increasing rate.

The action of pure Nitric acid on pure metals is often slow at first, gradually becoming faster, until it eventually may become very vigorous. Veley has shown that this increase of vigour is due to Nitrous acid formed in the reaction, acting autocatalytically. These are instances of Positive Autocatalysis.

The formation of lactones from hydroxy-acids is accelerated by the presence of acids, and the rate is proportional to the concentration of the Hydrogen ions (Hjelt, *Ber.*, 1891, 24, 1236; Collan, *Z. Phys. Chem.*, 1892, 10, 130). Now the hydroxy-acids themselves, though weak, are ionised to a small degree, so that in solution they are able to catalyse their own lactone formation. In producing lactone, however, the concentration of the hydroxy-acid, and therefore of the Hydrogen ions, is continuously diminishing. The rate of lactone formation therefore decreases, due to the catalyst becoming used up. This is an instance of Negative Autocatalysis.

Ostwald showed that the rate of spontaneous lactone formation from γ -Hydroxy-valeric acid :—



was much retarded by the addition of Sodium valerate. The addition of the salt reduced the electrolytic dissociation of the acid, and so diminished the rate of formation of lactone.

Bodenstein and Lind (*Z. Phys. Chem.*, 1906, 57, 168) found that the rate of combination of Hydrogen and Bromine was retarded by the Hydrobromic acid produced, and concluded that this was a case of negative autocatalysis in an homogeneous system.

Anticatalysis

The activity of a catalyst may be greatly altered by the presence of a foreign substance. When the effect of the foreign substance is to reduce the normal activity of a catalyst, it is described as an

Anticatalyst, or commonly, a Poison. The effects of anticatalysts may sometimes be so great that minute percentages are sufficient to suppress completely the functioning of a catalyst.

The anticatalytic action of a number of gases (Carbon monoxide, Ammonia, Sulphuretted hydrogen, Hydrochloric acid, Carbon disulphide, etc.) towards Platinum, in inducing combination between Hydrogen and Oxygen, was known to Turner, Henry, and Faraday, and some account of their investigations has already been given. Schönbein (*J. pr. Chem.*, 1843, 29, 238) noted that the hydrides of Sulphur, Selenium, Tellurium, Phosphorus, Arsenic, and Antimony all inhibited the action of Platinum in this and similar oxidising catalyses, and supposed the inhibition to be due to a film of Sulphur, Selenium, etc., forming on the Platinum.

The first patent for the manufacture of Sulphuric acid by atmospheric oxidation of Sulphur dioxide in contact with Platinum was taken out by Phillips as far back as 1831. Many attempts since made to apply this process on a large scale have been unsuccessful, owing to the Platinum rapidly losing its catalytic activity. Not until comparatively recently has the cause of this inhibition been traced and the process established. Minute traces of certain substances, especially Arsenic compounds, have been found to exert an inhibitory influence out of all proportion with their quantity. By using purified gases, free from dust, the "life" of the Platinum catalyst has become very long indeed.

It is probable that all catalyses, especially those in heterogeneous systems, are susceptible to anticatalytic influences, although the reduction of catalytic activity is generally not great. We shall have occasion to refer to many instances in later chapters. Striking instances of anticatalysis are the following :—

The Deacon process for the manufacture of Chlorine could not be established on a large scale until Hasenclever, in 1883, suggested a method of purification of Hydrochloric acid gas. The value of the process lay in employing it in conjunction with the Leblanc soda process, which produced large quantities of Hydrochloric acid as a bye-product. Made in this way, the Hydrochloric acid contained Sulphuric acid, which quickly poisoned the Cuprous chloride catalyst.

Sabatier found that catalytic Nickel was poisoned by a trace of halogens, Sulphur compounds, etc. On one occasion he left pure Phenol overnight in an open flask. The laboratory air contained Bromine fumes, and on the following day the Phenol could not be hydrogenated.

Iron is inert as a catalyst in the Haber Ammonia process unless it is specially purified from certain poisons, of which Sulphur is the chief.

The instances cited are chosen on account of the extreme action

exerted by the particular poisons. It is, however, very common for the activity of a catalyst to be retarded in some measure by anticatalytic impurities, a matter always to be considered when conducting a catalytic reaction. For example, it will influence the choice of support (if any) upon which the catalyst is mounted, the material of the apparatus, and the method of preparing or purifying the reactants. The importance of anticatalysts becomes especially marked in transferring a catalytic operation from a laboratory to a manufacturing scale.

Bancroft (*J. Phys. Chem.*, 1917, 21, 767) has examined the effect of a large number of anticatalysts on the following two reactions: (a) The decomposition of Hydrogen peroxide by Platinum, and (b) the decomposition of Hydrogen peroxide by Hæmase, the enzyme associated with Hæmoglobin, in blood. He measured the molecular concentration at which the anti-catalysts mentioned in Column 1 of the following table reduced the rate of catalytic decomposition approximately to one-half.

| Poison. | Colloidal Platinum. | Hæmase. |
|--|---------------------|-----------------------|
| | 1 Molecule in | 1 Molecule in |
| H ₂ S | 300,000 | 1,000,000 |
| HCN | 20,000,000 | 1,000,000 |
| HgCl ₂ | 2,000,000 | 2,000,000 |
| HgBr | — | 300,000 |
| Hg(CN) ₂ | 200,000 | 300,000 |
| Iodine | 5,000,000 | 50,000 |
| NH ₂ OH.HCl | 25,000 | 80,000 |
| Phenyl hydrazine | — | 20,000 |
| Aniline | 5,000 | 400 |
| As ₂ O ₃ | 50 | No poisoning at 2000. |
| CO | Very poisonous. | No poisoning. |
| HCl | 3,000 | 100,000 |
| NH ₄ Cl | 200 | 1,000 |
| HNO ₃ | } No poisoning. | 250,000 |
| H ₂ SO ₄ | | 50,000 |
| KNO ₃ | | 40,000 |
| KClO ₃ | | 40,000 |
| | Slight poisoning. | |

The same poisons therefore act in very different degrees towards different catalysts.

In some cases, a reactant or a product of reaction may possess an anticatalytic influence. Thus, Bodenstein showed that for the oxidation of Sulphur dioxide by Oxygen, in presence of Platinum, Sulphur trioxide is anticatalytic (*Z. Elektrochem.*, 1903, 9, 696), and Bodenstein and Ohlman found that the union of Carbon monoxide and Oxygen, in contact with quartz glass, was retarded by the Carbon monoxide (*Z. Phys. Chem.*, 1905, 53, 166). When the product of a reaction is very strongly anticatalytic, it may be anticipated that the amount of reaction (or the apparent equi-

librium) will depend on the amount of catalyst present, a small quantity of catalyst being poisoned sooner than a larger quantity. Neilson has described a case which Bancroft has explained in this way (*Amer. J. Physiol.*, 1906, 15, 148). The glucosides Salicin and Amygdalin, which yield Hydrocyanic acid among their scission products, are hardly attacked in presence of Platinum-black in a closed flask, on account of the poisonous action of the Hydrocyanic acid on the Platinum. In an open flask, on the other hand, from which the Hydrocyanic acid can gradually escape, scission slowly occurs.

Protective colloids used to stabilise colloidal solutions often reduce the catalytic powers of such solutions—though the reduced activity is more than compensated for by the great dispersion of catalyst which the protective colloid maintains. Groh found that the decomposition of Hydrogen peroxide by Platinosol was influenced as follows when Gelatin was used as protective colloid (*Z. Phys. Chem.*, 1914, 88, 414):—

| Per cent. of Gelatin. | Relative times required to decompose 50% of the H_2O_2 . |
|-----------------------|---|
| 0 | 100 |
| 0.001 | 437 |
| 0.01 | 460 |
| 0.05 | 620 |
| 0.1 | 983 |

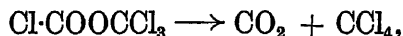
Rideal (*J. Am. C.S.*, 1920, 42, 740) and Iredale (*J.C.S.*, 1921, 119, 109) have observed similar instances.

The following two anomalous phenomena are explained by Bancroft as probable instances of catalytic poisoning (*J. Ind. Eng. Chem.*, 1922, 14, 447). In presence of excess of water, the hydrolysis of Phosgene proceeds rapidly to completion:—

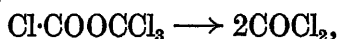


and the reaction is not reversible. Strong Hydrochloric acid, however, almost entirely suppresses the reaction. Bancroft suggests that in reality Phosgene and water only react in the presence of a catalyst—which may be the walls of the containing vessel—and that the effect of strong Hydrochloric acid is to poison the catalyst, achieving this by adsorption on the catalytic surface, thereby preventing access of the Phosgene and water. The remarkable stability of Phosgene clouds in moist air, it is suggested, may be due to the absence of a catalyst, necessary for interaction.

Trichloromethylchloroformate, $Cl \cdot COOCCl_3$, decomposes to Carbon tetrachloride and Carbon dioxide in presence of Alumina



and to Phosgene in presence of Ferric oxide,

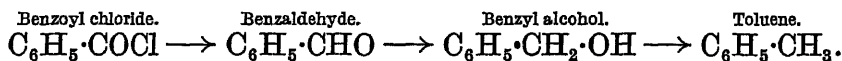


II Sc Lib B'lore
541.39 N
541.39
96

and the reverse actions have never been observed. Trichloromethyl chloroformate was placed in contact with Ferric oxide in a closed vessel connected with a manometer, and the rise of pressure, due to dissociation to two molecular equivalents of Phosgene, observed. Dissociation at first was rapid, but slackened and finally came to an end. Raising the temperature caused the reaction to recommence and to proceed a little farther, but it soon ceased, and no reversal occurred on reducing the temperature to the initial point. These results are consistent with the supposition that the Ferric oxide gradually becomes poisoned. Rise of temperature modifies the adsorption responsible for poisoning, so that a further quantity of Trichloromethyl chloroformate can make contact with the catalyst and decompose before further poisoning stops the reaction.

The properties of anticatalysts have been usefully employed by Rosenmund and his collaborators (*Ber.*, 1918, 51, 585, 594; 1921, 54 B, 425, 638, 1092, 2033, 2038, 2885, 2888; 1922, 55 B, 609, 2357, 2774; 1923, 56 B, 1481). During experiments which resulted in the discovery of a general method for the preparation of aldehydes from acid chlorides (see page 289), Rosenmund observed irregularities in the action of Palladium, and especially of Nickel catalysts, which were later traced to the influence of foreign materials. Abel (*Ber.*, 1921, 54 B, 1407; 1922, 55 B, 322) and Schliewinsky (*Z. angew. Chem.*, 1922, 35, 483) were unsuccessful in attempts to repeat Rosenmund's results, and erroneously concluded the method was unsatisfactory.

When Rosenmund attempted to hydrogenate Benzoyl chloride by his method, in presence of a Palladium catalyst, using chemically pure Benzene, Toluene, or Cymene as solvents, practically no Benzaldehyde was formed, a result attributed to the poisonous action of the solvent on the Palladium. The satisfactory results described in the first papers were obtained by the use of solvents not specially purified, from which it appeared that certain impurities were capable of countering the influence of anticatalysts. Developing the principle, it was shown that, by partial poisoning, a reaction could be directed along a desired course, or stopped at a certain stage, which, but for such control, would proceed otherwise. Thus, when Benzoyl chloride is hydrogenated in presence of Palladium, the following reactions occur successively :—



By variation of the solvent, and addition of foreign substances, it was found possible to confer such a degree of specificity upon the catalyst that the reaction stopped at either stage as desired.

To a reaction mixture, consisting of 2 grams of Benzoyl chloride

in 10 c.c. of pure Xylene to which 0.7 gram of palladinised Barium sulphate had been added (temperature about 150° C.), small quantities of foreign materials (Thiophene bromide, Quinoline, sulphurised Quinoline, Quinine, Dimethylaniline, Benzthiazine, Diphenyl disulphide, etc.) were introduced. In every case an increased yield of Benzaldehyde was obtained, the maximum, when sulphurised Quinoline was used as "adulterant," reaching 90 per cent. of the theoretical. Reduction stopped at the aldehyde stage, no alcohol or hydrocarbon being formed: the first recorded case of the artificial production of a specific catalyst by addition of a chemical "control."

The control can be exercised in such a way that reduction proceeds to the next stage, Benzyl alcohol, which reacts with excess of the acid chloride to give Benzyl benzoate. Under most conditions where reduction beyond the aldehyde was effected, bye-reactions also occurred leading to a mixture of products, but in boiling Toluene solution, with Xanthone as the chemical control, conditions were so adjusted that Benzyl benzoate was the main product.

Similar partial poisoning was shown also to influence the oxidation of alcohols to aldehydes. Thus, Benzyl alcohol in boiling Cymene solution gives only a low yield of Benzaldehyde (about 3 per cent. of theory) when air is passed, and this yield is hardly increased by addition of such catalysts as Copper, Silver, Magnesium, Platinum, Nickel, Aluminium, Zinc, Antimony, or Carbon. When, however, Quinoline also is added, then in the cases of Nickel, Silver, and Copper the catalyst is strongly activated; but differently in the three cases. Production of Benzaldehyde is favoured in the case of Copper, while in the cases of Nickel and Silver formation of Ether and other condensation products is induced.

The oxidising action of such catalytically excited Oxygen is further enhanced when a nitro-body, the best being meta-Dinitrobenzene, is added in addition to Quinoline, and Rosenmund developed a general mode of preparation of aldehydes from primary alcohols, and ketones from secondary alcohols, based on dehydrogenation in the liquid state, in presence of finely-divided Copper, Quinoline, a nitro-compound, and a current of Oxygen or air. Tertiary alcohols are not affected by this treatment. Aliphatic, aromatic, and heterocyclic aldehydes can be made in this way, and for the oxidation of non-volatile alcohols the method possesses considerable practical value, but offers no advantages over the older processes in the case of volatile alcohols. Benzhydrol in this reaction gives Benzophenone almost quantitatively, and Ethyl, Propyl, isoButyl and fermentation Amyl alcohols give their corresponding aldehydes: in yields diminished by the quantity of alcohol escaping by volatilisation in the current of air. ortho-Chlorobenzyl and Furfuryl alcohols likewise yield the aldehydes. The optimum temperature varies in

the different cases, from 125° C. for Amyl alcohol to 195° C. in the case of ortho-Chlorobenzyl.

A case of "protective poisoning" has been described by Palmer (*Proc. R.S.*, 1920, 98 A, 13). Below 300° C., pulverulent Copper dehydrogenates Ethyl alcohol to Acetaldehyde without formation of secondary products. If, however, the two products of the reaction, Acetaldehyde and Hydrogen, be passed over the same catalyst at 250–300° C., much of the aldehyde is decomposed. Palmer supposed that the aldehyde was stabilised in presence of alcohol owing to selective adsorption of the latter by the catalytic surface, thereby preventing contact with the aldehyde.

Explanations of anticatalysis all postulate some action of the anticatalyst whereby effective contact between the catalyst and reactants is hindered or prevented. This may be due to adsorption of the anticatalyst at the catalytic surface, or to simple mechanical or chemical causes. For example, some cases of poisoning are clearly brought about by chemical action between the poison and the catalyst, in which case the decay of activity is gradual, and cumulative. In other cases, the action is purely mechanical, as when a non-volatile solid or tarry material, perhaps formed in the reaction, is deposited on the catalyst.

Meyerhof (*Pflüger's Archiv*, 1914, 157, 251, 307) explained the "narcotic" action of alcohols and urethanes towards the decomposition of Hydrogen peroxide by colloidal Platinum by supposing that a surface film of the narcotic was formed over the particles of catalyst, preventing contact with the reacting substances. Alcohols and urethanes were also found by Meyerhof to retard the inversion of cane-sugar by the enzyme Invertase, and the same explanation was proposed, that the sugar was unable to gain access to the particulate surfaces of the colloidal enzyme.

In some cases, retardation of the action of a colloidal catalyst may be due to agglomeration of the colloid by the poison, which Bredig has shown to be possible (*Z. Phys. Chem.*, 1899, 31, 332). Ultramicroscopic examination proves, however, that this is not the explanation of the cases of "narcosis" observed by Meyerhof.

More recently, Langmuir has shown that his theory of adsorption suffices to explain catalytic poisoning in heterogeneous systems. The poison is adsorbed upon the catalyst, and held by chemical forces which are comparable in strength with those between catalyst and reactants. The active surface is therefore less accessible, and catalytic action slower. The theory is dealt with in Chapter IV.

Catalytic Promotion

We have seen that the activity of a catalyst is influenced by the presence of certain impurities, and have considered instances of

anticatalysis. Frequently the effect of an added impurity is to augment the activity of a catalyst, in which case it is termed a promoter or an activator.

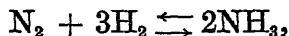
In general, the magnitude of the effect produced by a catalyst is in direct proportion to the amount of catalyst present. When a mixture of several catalysts is employed in a reaction, the total effect of the two is generally directly additive, that is, each catalyst induces its own action independently of the other. Many cases are known, however, in which this last statement does not hold. For example, Mercury sulphate and Copper sulphate both accelerate the oxidation of organic substances by boiling strong Sulphuric acid. Their combined effects are greater than the sum of their individual effects, so that one of the substances is promoting the action of the other. This, however, is not a typical instance of catalytic promotion, which is perhaps to be more truly regarded as the reverse of anticatalysis. Thus, substances exerting little or no catalytic action of their own, when mixed with a catalyst, sometimes in very small proportions, may markedly increase its action. A promoter may therefore be aptly described as a positive catalyst of a catalyst, while a poison is a negative catalyst of a catalyst. ✓ Taylor and Pease (*J. Phys. Chem.*, 1920, 24, 241) define catalytic promotion as "those cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the supposition that each substance in the mixture acts independently and in proportion to the amount present."

Ipatiev (*Ber.*, 1910, 43, 3387) found that Amylene was one-third converted into isoPentane in 28 hours, by means of Hydrogen at 200 atmospheres and 300° C., in contact with Copper oxide in a Copper tube, while under the same conditions, in an Iron tube, the conversion was complete in 12 hours.

The formation of Hydrogen from Carbon monoxide and steam (or water gas and steam) is catalysed by Iron, Nickel, or Cobalt, or the oxides of these metals. The activity of these catalysts can, however, be much increased by admixture with oxides of Chromium, Thorium, Uranium, Beryllium, or Antimony, and very small quantities of these latter oxides may exert a very considerable influence (Badische, E.P. 27963 of 1913). It was in this connection that the term "promoter" was first used (Badische, E.P. 19249 of 1910).

A mixture of Copper oxide and Manganese peroxide, made by precipitation, slowly induces the union of Carbon monoxide and Oxygen at the ordinary temperature. If 1 to 5 per cent. of an oxide of Cerium is added to the oxides of Copper and Manganese, the combination of the two gases is effected at a much greater speed.

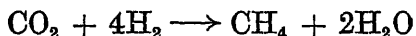
The equilibrium between Nitrogen, Hydrogen, and Ammonia,



is attained with moderate speed in presence of finely-divided Iron, free from poisons. The activity of Iron in this respect is, however, much increased if small quantities of Molybdenum, Tungsten, or Uranium be added.

The patent literature contains many references to promoters, and it is probable that most catalytic reactions—especially those in heterogeneous systems—are capable of activation in some measure. In particular, efforts have been made to replace expensive metals, and substances highly susceptible to the action of poisons (*e.g.*, Platinum), by commoner agents, activated by addition of promoters. For example, many catalysts have recently been proposed for the manufacture of Sulphuric acid from Sulphur dioxide and air.

Various attempts have been made, but with indifferent success, to explain the phenomena of catalytic promotion. It is established that in many cases the addition of a promoter so alters the surface of a catalyst that its adsorptive powers for one, at least, of the reactants is increased. Russell and Taylor, discussing the catalytic action of Nickel, promoted by Thoria, in the reaction



suggest that increased adsorption might be brought about as follows ✓ (*J. Phys. Chem.*, 1925, 29, 1325). The unsaturated metal atoms which are assumed to be responsible for catalytic action (see Taylor's modification of Langmuir's theory, Chapter IV) are present in pure Nickel in higher concentration the lower the temperature at which the Nickel is reduced. These coalesce as the temperature of reduction rises, but the presence of Thoria in supported Nickel catalysts prevents this, and by forming Nickel-Thoria interfaces increases the concentration of these atoms.

In connection with the chemical theory of catalysis, it has been suggested that while the catalyst forms an intermediate compound with one reactant, the promoter does so with the other, the two intermediate compounds then reacting. If this view were correct, then the catalyst and promoter should be interchangeable, and it is difficult to understand why a small proportion of promoter should produce a considerable influence.

To explain the effect of promoters in the Ammonia synthesis, it has been suggested that while Iron is capable of forming both a hydride and a nitride, and is therefore a catalyst, a mixture of Iron with Molybdenum, or other promoter, forms hydrides and nitrides in proportions nearer to those stoichiometrically requisite for subsequent resolution into Ammonia.

✓ Medsforth (*J.C.S.*, 1923, 123, 1452) suggests three possible modes of action of promoters: (1) They may facilitate decomposition of intermediate compounds. (2) They may induce combination among the reacting substances to form an intermediate complex which is decomposed by the catalyst. (3) They may adsorb one of the reactants, and produce thereby a greater concentration in contact with the catalyst.

From the results of his experiments on the reduction of oxides of carbon in contact with Nickel, Medsforth regarded the third explanation as the most probable.

Pulsating Catalysis

The periodicity of some chemical reactions presented very puzzling features to earlier investigators. Joubert in 1874 noticed that the luminosity of Phosphorus was periodic when it was confined in an exhausted vessel and air allowed slowly to leak in. Weiser and Garrison (*J. Phys. Chem.*, 1921, 25, 61) explained this by supposing the alternate formation and dissolution of an oxide film.

Periodicity is most easily observed in reactions where gases are evolved, and most of the instances recorded refer to reactions of this type. There are grounds, however, for supposing that under certain circumstances the phenomenon is a very general one, the reaction velocity commonly being smoothed out by superposition in a reaction mixture of all the different phases of periodic action.

Bredig and Weinmayr (*Z. Phys. Chem.*, 1903, 42, 601) showed that the decomposition of Hydrogen peroxide in alkaline solution in contact with a metallic Mercury surface was periodic. The concentration of alkali most conducive to periodicity was between 10^{-3} and 10^{-4} normal. Excess of alkali, or acid, stopped the periodicity, and it was much modified by traces of foreign bodies and other influences. For example, Bredig and Wilke regulated the periods by passing a direct or an alternating current through the Mercury (*Biochem. Z.*, 1908, 11, 67; see also Bredig and von Antropov, *Z. Elektrochem.*, 1906, 12, 585). The cause of this periodicity was shown by Fredenhagen (*Z. Elektrochem.*, 1907, 13, 859) and by von Antropov (*Z. Phys. Chem.*, 1908, 62, 513; *J. pr. Chem.*, 1908, 77, 273) to be due to the periodic formation and decomposition of a film of golden-coloured oxide (probably the explosive HgO_2 , isolated by von Antropov) on the Mercury surface. This film, under certain conditions, can be seen by the eye to form and disappear intermittently.

Almost all the known instances of periodic action are in heterogeneous systems, one component of which is a metal. Two cases only are known in homogeneous systems, as follows: Bray (*J. Am. C.S.*, 1921, 43, 1262) found that the evolution of Oxygen in the

action between Hydrogen peroxide and Iodic acid was periodic in presence of Sulphuric acid. Morgan (*J.C.S.*, 1916, 109, 274) found that when Formic acid was decomposed with strong Sulphuric acid at 50–60° C., the evolution of Carbon monoxide was periodic, periods of action being followed by periods of complete inaction. The periods were destroyed when broken porcelain was added, and it was suggested that the phenomenon was due to supersaturation of the liquid with gas, which periodically gave off the excess dissolved in it. It was then found, however, that pure acids did not show this periodicity, but that addition of a trace of alcohol sufficed to induce it. The idea of supersaturation clearly will not account for this.

Plotnikov (*Z. wiss. Photochem.*, 1919, 19, 22) found that the concentration of Chlorine varied periodically when a solution of Chlorine in Carbon tetrachloride was exposed to ultra-violet light. The nature of the reactions involved was not suggested.

The solution of metals in acids furnishes the most distinctive examples of periodic chemical action. Ostwald obtained well-defined periods in the solution of Chromium in Hydrochloric acid (*Z. Phys. Chem.*, 1900, 35, 33, 204; *Phys. Z.*, 1900, 1, 88), and Banerjee and Dhar (*Z. anorg. Chem.*, 1922, 122, 73) noticed the same when an Iron–Nickel alloy was dissolved in 50 per cent. Nitric acid. Ostwald showed that increasing the concentration of the acid, or raising the temperature, increased the frequency of the periods. Addition of oxidising agents brought about the same result, while Formaldehyde or Potassium cyanide reduced the frequency, and in sufficient concentration stopped the periodicity altogether. After using all his Chromium, Ostwald was unable to repeat his results with later samples, the evolution of gas being quite regular. He concluded that an impurity was responsible for the periodicity in the earlier experiments, but his search for this suspected catalyst was only partially successful.

The rate of solution of metals has been systematically investigated by Hedges and Myers (*J.C.S.*, 1924, 125, 604; 1925, 127, 445), who have added many instances of periodic action to those already known. Their results indicate, in fact, that it is of very common occurrence. The rate of formation of Hydrogen was recorded automatically and continuously in the following reactions: solution of Manganese, Cadmium, Zinc, Iron, Aluminium, and Magnesium in Hydrochloric acid; Sodium and Alcohol, Sodium amalgam and water, Calcium and water, Aluminium and Cupric chloride, Aluminium and Alkalies, and autoxidation of Chromous chloride in presence of Platinum. In all cases, the rate of evolution of the Hydrogen varied periodically with the time. This was essentially a feature of the reaction, supersaturation of liquid with

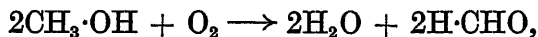
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the gas being proved to play no part. Moreover, the periodicity was due to different relative rates of reaction, the pulses being superimposed on the ordinary reaction curves, and not to alternate reaction and cessation of reaction, or periods of activity alternating with periods of passivity. This was regarded as indicating that the reaction was catalysed at regular intervals of time, a view which further experiments confirmed. After a number of experiments, periodicity ceased to be obtained, and Hedges and Myers concluded, like Ostwald, that it depended upon the presence of a third substance. The quantity of the third substance, or catalyst, necessary was evidently very small, since in the original experiments it could only have gained access by presence in the glass vessels used, while in Ostwald's experiments it must have occurred as impurity in the metal. After many experiments, Hedges and Myers succeeded in inducing periodicity artificially by the addition of a catalyst, which periodically augmented the regular reaction. The catalysts found were either colloids, or a second metal, which was always more effective after treating in such a way as to expose a clean, crystalline surface. An electrolytically or electrochemically deposited metal was most effective of all.

No explanation of pulsating catalysis has been hazarded. It is evident that it must depend upon the existence of active and inactive periods of a catalyst, and not upon any peculiar property of the reactants, since this, if it existed, would be beyond our means to detect. Thus, all phases of a periodic mechanism would exist simultaneously in a reaction mixture if the properties of the reactants only were involved, and the effect measured would be that of a very large number of superimposed periodic actions in which no simple pulses could be distinguished.

The Specific Properties of Catalysts

Some reactions are induced by almost any contact agent, *e.g.*, oxidation of Methyl alcohol to Formaldehyde,



or decomposition of Acetic acid to Acetone,



A wide choice of efficient catalysts is available for either of these reactions, and most substances assist them to a certain degree. More generally, however, a reaction can only be satisfactorily realised by a few catalytic agents, which therefore possess certain specific properties conducive to that reaction. Each reaction requires its own specific catalyst, which varies much in action

according to its mode of preparation and treatment, and other conditions which determine its surface form.

When a mixture of Naphthalene and air is passed over various heated contact agents, a complex mixture of solid, tarry, and gaseous products usually results, containing traces of Phthalic anhydride. When, however, the contact material is Vanadium pentoxide, a very clean decomposition of the Naphthalene into Phthalic anhydride is obtained. Molybdenum oxide and Tungstic oxide also induce this reaction, but less cleanly. Vanadium pentoxide therefore possesses certain specific catalytic properties for the reaction :—



while Molybdenum and Tungsten oxides also possess properties in common, but to a less degree.

It is in the action of enzymes that the most remarkable instances of specificity occur. For each reaction, there is a corresponding enzyme, and it frequently happens that this enzyme is effective for the one reaction only. The extraordinary selectivity of "organised ferments" was recognised by Pasteur (1860), who found that the two enantiomorphous forms of Ammonium tartrate were assimilated by the mould fungus, *Penicillium glaucum*, at widely different rates, and based on this observation his well-known method of obtaining pure lævorotatory Ammonium tartrate from Ammonium racemate.

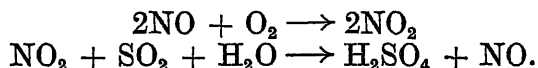
By the action of Alcohols on Glucose, in presence of Hydrochloric acid, Fischer prepared a series of artificial glucosides. Since the formation of the glucoside introduces an additional centre of asymmetry in the glucose molecule, two stereoisomeric glucosides (designated α and β) were always formed simultaneously. Fischer found that Maltase attacked the α -glucosides, but had no action on the stereoisomeric β -glucosides, while Emulsin hydrolysed the β , and did not touch the α .

Scope of the Subject of Catalysis

Till within comparatively recent times catalytic reactions were regarded as exceptional, and this view seems to have been current right up to the time of its complete reversal by Ostwald, who defined catalysis in terms of reaction velocities, and found that most substances, if not all, in this sense were capable of functioning as catalysts. The speed probably of all chemical reactions is in some measure influenced by the presence of foreign materials. Armstrong in his theory of "Reversed Electrolysis" has, in fact, carried this view to the point of supposing that pure substances cannot interact, which implies universal catalysis.

Noyes and Sammet (*J. Am. C.S.*, 1902, 24, 498) classified catalysts as follows :—

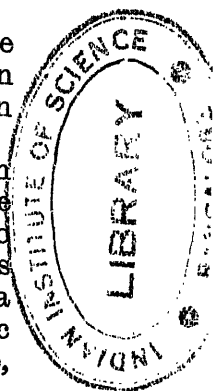
1. *Carriers*, or agents which are known to accelerate reactions through formation of an intermediate compound with one of the reactants. In some cases, intermediate stages in a reaction can be distinguished, and carried out independently. The function of the catalyst then seems evident. For example, in the "Lead Chamber" process for Sulphuric acid the net result is the oxidation of Sulphurous to Sulphuric acid by air, in presence of Nitric oxide as carrier. The oxidation can, however, be actually carried out in the following stages :—



In the majority of cases, however, the intermediate stages are less apparent, and sometimes uncertain: *e.g.*, Chlorination in presence of a "Chlorine carrier," use of Aluminium chloride in organic syntheses, etc.

2. *Adsorbent Contact Agents*, or substances which induce reaction by contact of substances at their surface. This class includes the very numerous reactions which gases and vapour may be made to undergo by contact with a solid surface. Many remarkable changes can be effected in this way, the catalyst commonly exhibiting a highly specific action: *e.g.*, Hydrogenation in presence of catalytic Nickel, partial combustion in presence of Vanadium pentoxide, dehydration in presence of Alumina, Thoria, etc.

It is probable that reactions between gases are always aided by contact with solid surfaces at a suitable temperature, as, for example, in the phenomena of surface combustion. In many cases gas reactions occur mainly at the surface of the containing vessel, which therefore adopts a catalytic function. For example, Van 't Hoff heated a mixture of Hydrogen and Oxygen to 440° C. in glass bulbs ("*Études*," p. 52), and Meyer, Krause, and Askenasy (see *Lieb. Ann.*, 1892, 269, 49) repeated these experiments at 518°. The rates of reaction in each case were abnormal, and different bulbs gave inconsistent results, evidently due, as Bodenstein subsequently proved (*Z. Phys. Chem.*, 1899, 29, 665), to the different catalytic powers of the glass in the several cases. Bodenstein, using porcelain vessels, obtained more consistent results, which indicated a rate of reaction approximately proportional to the area of the porcelain surface. The formation of water, therefore, occurred at the surface of the porcelain only, and not in the interior of the gas. Bone and Wheeler, in a much more careful investigation of this reaction (*Phil. Trans.*, 1906, 206, 1), using many different surfaces, showed that the catalytic powers of new surfaces increased



to a maximum, and having acquired a steady value, induced a rate of reaction proportional to the pressure of the gases.

Experiments by Van 't Hoff and Kooy showed that, contrary to expectation, the rate of decomposition of Arsine,

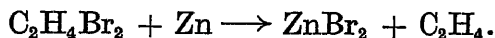


was directly proportional to its pressure so long as the temperature was constant. The probable explanation is that decomposition takes place exclusively at the surface of the containing vessel. Its rate is therefore proportional to the number of molecular impacts per unit of time with the surface, and this, in turn, is proportional to the pressure of the gas. Cohen, heating Arsine in an enclosed vessel, showed that the rate of decomposition did not become steady until the internal surface of the vessel had become coated with Arsenic, which therefore behaves autocatalytically (*Z. Phys. Chem.*, 1896, 20, 303; 1898, 25, 483).

Reactions of a very different type, which must also be regarded as effected by the agency of surface adsorption, are those in which a gas, at ordinary or increased pressure, reacts with a liquid containing a finely-divided catalyst in suspension, *e.g.*, hydrogenation by the methods of Paal, Willstätter, and Ipatiev, and hydrogenation of oils. A finely-divided, suspended catalyst often facilitates the decomposition of dissolved substances, especially when the reaction involves the disengagement of gas, such as decomposition of Hydrogen peroxide, and the action of Copper powder on dissolved Diazo-compounds.

3. *Electrolytic Contact Agents.* Reactions in which metals are involved are often accelerated by the presence of a substance which completes a voltaic circuit. Thus, action between a pure metal and a pure acid is frequently slow, *e.g.*, Zinc and dilute Sulphuric acid, or Tin and strong Hydrochloric acid. In both cases, however, action is very fast if certain impurities are present, as, for example, if commercial granulated Zinc is used in the former case, or if a few drops of Platinic chloride solution are added in the latter.

Ethylene dibromide has no action on granulated Zinc alone. If a little Copper chloride is added, in a few seconds the following reaction sets in with very brisk effervescence :—



4. *Water.* The action of water is probably unique. It seems to be required, at least in traces, for most reactions. Dixon, and, later, Baker, have shown that completely dried gases are inert, even in cases where violent or explosive action takes place, if minute traces of water are present. For example, neither Hydrogen nor Carbon monoxide will explode with Oxygen, when the gases are

dry, unless a very powerful discharge is used in the mixture, and even then combination is incomplete. Phosphorus can be distilled in dry air, and burning metallic Sodium is extinguished by plunging into Chlorine, dried over Phosphoric anhydride. Ammonia and Hydrochloric acid do not combine when both gases are dry, and dry Ammonium chloride is not dissociated on vaporising, as is proved by its normal vapour density in this case. Still more recently, Baker has shown that the boiling points of liquids and the melting points of solids are affected in an extraordinary manner by very prolonged drying.

Water is also essential to most reactions between solids and liquids. This is sometimes by virtue of its solvent action (*e.g.*, Ionic reactions), but its presence is often necessary in small quantities before a reaction can take place in a non-aqueous solvent. For example, Iodine and Sulphuretted Hydrogen react very slowly in dry Ether, but in presence of a trace of water action is very fast.

5. *Dissolved Electrolytes.* Three kinds of action are possible : (a) In which Hydrogen, Hydroxyl, or other ions are catalysts, as in saccharification of starch by acids, hydrolysis of esters by acids, hydrolysis of nitriles by acids or alkalies, and condensation of Benzaldehyde to Benzoin in presence of the Cyanide ion. (b) Coagulation of colloidal solutions and emulsions due to the ionic charges. (c) Retardation of reactions involving weak acids, in presence of a neutral salt of that acid.

6. *Enzymes.* The number of enzyme actions now known, effected either in presence of a living organism or by the enzyme independently, is now very great, and is continually increasing with the advance of biochemistry. Not only are the processes of fermentation, putrefaction, and animal digestion to be included in this class, but also, in most probability, a number of much more complicated biochemical changes which take place within the living organism. The principle of reversibility of enzyme actions, established by Croft Hill, may be involved in some of these processes.

7. *Inorganic Colloids.* The activity of a solid catalyst is more marked the greater its degree of subdivision. In the colloidal state, this fineness of division reaches its limit for a heterogeneous system, so that colloidal substances are usually more active catalysts than the same substances in a coarser form. Examples of the use of colloids are Paal and Skita's methods of hydrogenation, decomposition of Hydrogen peroxide or diazo-compounds by colloidal metals, etc.

Other actions which must be regarded as within our scope, and not included in Noyes and Sammet's classification, are the following :—

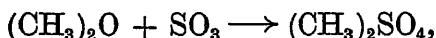
The rate and temperature of vulcanisation of rubber are greatly altered by the presence of small percentages of "accelerators."

The presence of substances in an electrolytic bath may greatly affect the course of chemical action at the electrodes, and widely different proportions of products result according to the presence or absence of such substances.

Influence of Solvents

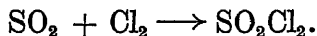
The rate of interaction between substances in solution is considerably influenced by the solvent, which therefore comes within our definition of a catalyst. It is probable that all reactions are influenced in some degree by the choice of solvent. Many instances could be given to show that an action which is slow in one medium may be rapid in another—*e.g.*, the solution of Magnesium in alkyl or aryl halogen compounds, which is much more rapid in Ether than in other common solvents. The following two reactions, important technically, are striking instances of the power of a solvent to assist interaction.

Manufacture of Dimethyl Sulphate. Dimethyl sulphate is made by the direct union of Dimethyl ether and Sulphur trioxide,



and is most easily effected by using Dimethyl sulphate itself as the solvent for the two reactants. Dimethyl ether and Sulphur trioxide are both miscible with Dimethyl sulphate, and heat is generated by mixing. By passing the reactants, either alternately or together, into water-cooled Dimethyl sulphate, combination takes place rapidly and smoothly, with formation of a very pure product.

Manufacture of Sulphuryl Chloride. Sulphur dioxide and Chlorine do not react easily when mixed, but in presence of certain solvents, which act catalytically, union is rapid and smooth:—



The usual catalyst is Camphor. When Sulphur dioxide is added to solid Camphor, absorption is rapid, and the Camphor melts to a pale yellow liquid. If Chlorine is now passed into this liquid, it is rapidly taken up, with formation of Sulphuryl chloride. Sulphur dioxide and Chlorine can be passed alternately many times before working up the product by distillation. The yield of Sulphuryl chloride is nearly theoretical, it is easily purified by redistillation, and the recovery of Camphor is complete. Sulphur dioxide treatment must always come first, and excess may be used at each stage without any disadvantage. Excess of Chlorine should be avoided.

According to E.P. 12861 of 1901, Sulphur dioxide and Chlorine, both in the liquid state, are made to interact in presence of Camphor, glacial Acetic acid, anhydrous Formic acid, etc. For example, Camphor is dissolved in liquid Sulphur dioxide in a closed vessel,

which is then well cooled, and the requisite quantity of Chlorine added. The product is obtained pure by distillation.

A systematic investigation of the influence of solvents in a chemical reaction was carried out by Menschutkin (*Z. Phys. Chem.*, 1887, 1, 611; 1890, 6, 41), who measured the rate of the reaction

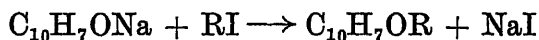


in twenty-three different solvents. Triethylamine and Ethyl iodide in equimolecular proportions (1 volume) were added to the various solvents (15 volumes) and the mixtures sealed in glass tubes and heated to 100° C. for various measured times. The progress of the reaction was followed by titrating the amount of base. It was found that in each solvent the reaction proceeded to completion at a rate corresponding with the law for dimolecular reactions. The value of the speed constant, however, differed very widely for the different solvents, as follows:—

| Solvent. | Speed Constant (Dimolecular). | Solvent. | Speed Constant (Dimolecular). |
|---------------------|----------------------------------|----------------------|----------------------------------|
| Hexane . . . | 0.00018 | Methyl Alcohol . . . | 0.0516 |
| Heptane . . . | 0.000235 | Ethyl Alcohol . . . | 0.0366 |
| Xylene . . . | 0.00287 | Allyl Alcohol . . . | 0.0433 |
| Benzene . . . | 0.00584 | Benzyl Alcohol . . . | 0.133 |
| Ethyl Acetate . . . | 0.0223 | Acetone . . . | 0.0608 |
| Ethyl Ether . . . | 0.000757 | | |

The presence of a hydroxyl group, or of an unsaturated linking in the solvent molecule, therefore appears to increase the reaction velocity, and in homologous series the velocity decreases with increasing molecular weight. Menschutkin attempted to correlate these velocity constants with various physical constants of the solvent, but without any very considerable success. The constants follow roughly the order of the Specific Inductive Capacities of the solvents in question, but the correspondence is not general. On the whole, those solvents which exert the greatest dissociating power on dissolved substances (and this property is related to the Specific Inductive Capacities) also show the highest velocity constants.

The velocity constants between Sodium β -naphthoxide and Methyl, Ethyl, and normal Propyl iodides were measured by Cox, using fifteen different alcohols as solvents,



(*J.C.S.*, 1920, 117, 493).

The naphthoxide was made by adding the calculated quantity of β -Naphthol to Sodium ethoxide, evaporating *in vacuo*, recrystallising the product from the smallest possible quantity of boiling

Acetone, and drying at 150° C. The reactions gave satisfactory constants for dimolecular reactions, and at $\frac{N}{I}$ concentration of reactants and a temperature of 50.5° C. were as follows :—

| Alcohol. | Methyl iodide. | Ethyl iodide. | <i>n</i> -Propyl iodide. |
|--------------------------|----------------|---------------|--------------------------|
| Methyl | 0.0459 | 0.0130 | 0.00567 |
| Ethyl | 0.0941 | 0.0212 | 0.00859 |
| <i>n</i> -Propyl | 0.0643 | 0.0127 | 0.00507 |
| <i>n</i> -Butyl | 0.0528 | 0.0107 | 0.00379 |
| <i>n</i> -Amyl | 0.0298 | 0.0052 | 0.00194 |
| isoPropyl | 0.0975 | 0.0177 | 0.0062 |
| isoButyl | 0.0635 | 0.0113 | 0.0037 |
| sec.-Butyl | 0.0571 | 0.0107 | 0.0037 |
| tert.-Butyl | 0.0350 | 0.0050 | 0.0015 |
| isoAmyl | 0.0392 | 0.0065 | 0.0020 |
| sec.-Amyl | 0.0332 | 0.0046 | 0.0017 |
| tert.-Amyl | 0.0114 | 0.0016 | 0.0005 |
| Allyl | 0.0381 | 0.0056 | 0.0020 |
| Benzyl | 0.0357 | 0.0078 | 0.0024 |
| Ethylene glycol . . | 0.0578 | 0.0014 | 0.0043 |

It will be seen that for the normal alcohols (with the exception of Methyl alcohol, which, as in many respects, is subnormal), there is a gradual and fairly regular decrease in the velocity constant with increasing molecular weight, suggesting that the value of *K* is additive for homologous series, and only slightly constitutive, the additive value somewhat diminishing as the series is ascended. Iso-, secondary, and tertiary alcohols show the same diminution as the series is ascended in the same class of alcohols: thus, the order of decreasing activity is isoPropyl, isoButyl, isoAmyl.

Alcohols with a branched chain ("iso"-alcohols) are more favourable media than the normal isomerides, and secondary alcohols are more favourable than the isomeric tertiary, but rather less than the isomeric iso-primary. For a given molecular weight of alcohol, the order of decreasing activity is iso-, secondary-, normal-, tertiary.

The quantitative results support the conclusion that had already been reached by Patterson and Montgomerie (*J.C.S.*, 1912, 101, 26, 2100) that variation of the solvent influences different reactions in a similar manner. Thus, a given set of solvents may hasten a particular reaction in a certain sequence. This same sequence holds throughout many different reactions, but Cox's figures show that though the sequence of activity is the same for the three iodides, the differences in activity cannot be represented by a constant factor. For a temperature arbitrarily fixed at 50.5° C. for each reaction, such a definite relation could, perhaps, hardly be expected.

The foregoing survey of the field of catalysis shows how diverse

are the types of chemical change that are classed as catalytic. On these grounds alone it is difficult to resist the conclusion that many reactions which are in no way fundamentally related have been classed together simply because they possess the one feature in common, that a component of the reacting system is recoverable *in toto* when the change is completed. Advance of knowledge may well show that catalytic phenomena should be sub-divided into many classes, each depending upon a distinct chemical or physical principle.

CHAPTER III

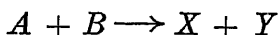
PHYSICO-CHEMICAL THEORY

The Law of Mass Action. Concentration. Rate of Reaction. Monomolecular, Dimolecular, and Trimolecular Reactions. Application of the Law of Mass Action to Equilibria in (a) Homogeneous, (b) Heterogeneous Systems. Influence of Temperature on Equilibrium. Principle of Le Chatelier. Van 't Hoff's Equation ("Isochore"). Nernst's Heat Theorem.

τ We have seen in the preceding chapter that chemical reactions comply with the same quantitative laws in the presence of a catalyst as in its absence. A brief study of these laws is now necessary, since with their help it is possible to predict many facts concerning any particular reaction, without recourse to experiment, from known physico-chemical data alone. Much guidance can therefore be obtained in experimental research, and time saved, especially when it is desired to be^{ing} about a new reaction by catalytic means.

The Law of Mass Action

According to the Law of Mass Action, the rate of chemical change at constant temperature is directly proportional to the product of the active masses, or concentrations, of the reacting substances. Thus, in the reaction



if the concentrations of A and B are represented by $[A]$ and $[B]$, then the rate of reaction at any instant will be proportional to the product $[A][B]$, and therefore equal to $[A][B]K$, where K is a constant, which we can describe as the velocity constant of the reaction. In general, K increases with rising temperature, and is also influenced by the presence of foreign materials, which accordingly assume the functions of positive or negative catalysts.

✓ *Concentration.* In solution, the concentration is generally measured in terms of gram-molecules per litre. The same units can be employed for gases, but it is generally more convenient in gaseous reactions to define the concentrations in terms of pressures. Since the concentration of a gas is directly proportional to its partial pressure, if A and B are gases, and P_A and P_B represent their partial pressures, respectively, the rate of reaction between them will be $K \cdot P_A \cdot P_B$.

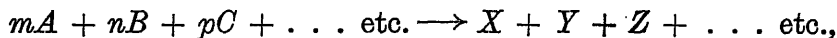
Rate of Reaction, rate of chemical change, or reaction velocity. This is generally measured in terms of quantity (gram-molecules) of substance changed per unit of time, that is,

$$\text{Rate} = \frac{\text{gram-molecules per litre undergoing change}}{\text{time}}.$$

Since the concentration of a reactant in a chemical change, and therefore also the rate of reaction, are continually diminishing as the change proceeds, it becomes necessary to specify each for a particular instant. In the notation of the calculus, if at the end of time t an infinitely small quantity dA of a substance changes in an infinitely short interval of time dt , the rate of change at time t is $\frac{dA}{dt}$, or, if dC represents the fall of concentration in the same time

interval, then the rate of change at time $t = \frac{dA}{dt} = -\frac{dC}{dt} = KC$.

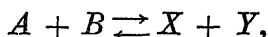
More generally, in the reaction



the rate of reaction at any instant will be equal to the product

$$[A]^m[B]^n[C]^p \times \dots \text{etc.}, \times K.$$

Reversible Systems. In reversible systems, two reactions are occurring simultaneously, the forward and the reverse, each with a distinct reaction velocity. Thus, in the reversible system



the forward action will take place at a speed

$$= K_1[A][B]$$

and the speed of the reverse will be

$$= K_2[X][Y].$$

At the point of equilibrium these two speeds will balance, that is,

$$K_1[A][B] = K_2[X][Y],$$

or
$$\frac{K_1}{K_2} = \frac{[X][Y]}{[A][B]}.$$

The ratio of the two constants $\frac{K_1}{K_2}$ may be more conveniently replaced by a single constant K , which is now called the Equilibrium Constant for the reversible reaction.

Monomolecular, Dimolecular, Trimolecular (etc.), Reactions

Consider the case of a reaction in which a single molecule of a substance A is undergoing change. If $[A]$ is the original concentration, and x is the amount changed at the end of time t , we have

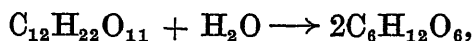
$$\frac{dx}{dt} = K([A] - x),$$

which gives on integration

$$K = \frac{1}{t} \log_e \frac{[A]}{[A] - x}.$$

A reaction involving one molecule only is a "monomolecular" change, and the velocity constant can be determined by measuring t , $[A]$, and x , and applying the above formula.

The inversion of cane-sugar in dilute water solution,

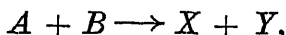


is an instance of a monomolecular reaction. Actually two molecules take part in the change, but in dilute solution the concentration of the water can be regarded as constant, so that the relation

$$-\frac{dC}{dt} = K([A] - x)$$

should hold. This was verified experimentally by Wilhelmy and later investigators, who found that in dilute aqueous solution the rate of inversion of cane-sugar at any instant was directly proportional to the concentration of unchanged cane-sugar.

If two molecules take part in a reaction, *e.g.*,



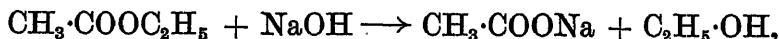
and if A and B be present in equimolecular quantities so that $[A]$ represents the concentration of both: then if x is the amount changed in time t

$$\frac{dx}{dt} = K([A] - x)^2,$$

which gives on integration

$$K = \frac{1}{t} \cdot \frac{x}{[A]([A] - x)}.$$

Reactions involving two molecules are "dimolecular." An example is the saponification of Ethyl acetate by means of caustic Soda,



the rate of which is found experimentally to follow the quantitative law just formulated.

Similarly, if three molecules react, we have

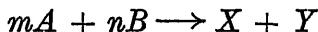
$$\frac{dx}{dt} = K([A] - x)^3$$

and

$$K = \frac{1}{t} \cdot \frac{x(2[A] - x)}{2[A]^2([A] - x)^2}.$$

These are "trimolecular" reactions.

The order of a reaction may therefore be determined by counting the number of molecules, whether alike or different, entering into reaction. Thus, the reaction



should be of the $(m + n)$ th order. In actual fact, however, it is found that for the vast majority of reactions, when values of K are measured, they comply with the formula for either a mono- or a di-molecular reaction. It is very rare that measurements of velocity indicate a reaction of higher order than the second. The explanation is simple. The greater the number of molecules that must be assembled in mutual contact for reaction to occur, the less likely it is to happen. Reactions of the third order are therefore much less frequent than those of the second order, while reactions of the fourth order, necessitating simultaneous contact between four molecules, are very scarce. Reactions involving interaction between a number of molecules in most probability therefore occur in a series of monomolecular or dimolecular stages, and the reaction velocity as measured is that of the slowest mono- or di-molecular reaction of the series. A value of K is therefore found which corresponds with a reaction of the first or second order.

From the foregoing, it will be seen that the state of a reaction at any instant can be calculated if we know (1) the order of the reaction, (2) the value of the velocity constant at the working temperature, (3) the concentrations of the reactants. The order of the reaction can be ascertained by either of the following methods: (a) Determine the concentrations of the reactant for a series of time intervals, and ascertain which formula gives a constant value for K . (b) Alter the concentrations and determine the corresponding rates of reaction. Let R_1 and R_2 be the rates at concentrations C_1 and C_2 . Then if

$$\frac{R_1}{R_2} = \frac{C_1}{C_2}$$

the reaction is monomolecular, while if

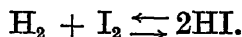
$$\frac{R_1}{R_2} = \left(\frac{C_1}{C_2}\right)^2$$

the reaction is dimolecular, and so on.

Equilibrium. A reversible reaction tends always to attain a state of equilibrium. Often the equilibrium will correspond with almost complete reaction in one direction, in which case the simple formulæ we have just developed can be applied directly without sensible error. Equilibrium, however, is almost always displaced by an alteration of temperature, so that a reaction which may be nearly completed at one temperature becomes far otherwise when the temperature is changed. For example, in presence of a catalyst and excess of air Sulphur dioxide is nearly completely oxidised to Sulphur trioxide at temperatures below 500°C. , but at higher temperatures the equilibrium becomes increasingly moved towards a mixture of Sulphur dioxide and Oxygen.

We shall now apply the Law of Mass Action to determine equilibria in reversible systems, and show how it enables us to calculate the effect of changing concentrations.

1. *The Equilibrium between Hydrogen, Iodine, and Hydriodic Acid.*



Suppose equal volumes, 1 gram-molecule of each, of Hydrogen and Iodine are mixed and raised to a certain temperature. When equilibrium is established, suppose x gram-molecules of each has combined. Two x gram-molecules of Hydriodic acid will then be formed. Let the total volume be V .

At equilibrium, the speed of the forward reaction will be

$$\frac{K_1(1-x)^2}{V^2},$$

and the speed of the reverse will be

$$K_2\left(\frac{2x}{V}\right)^2.$$

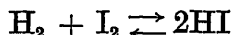
$$\therefore \frac{K_1(1-x)^2}{V^2} = \frac{4K_2x^2}{V^2}.$$

$$\begin{aligned} \text{Hence } K, \text{ the equilibrium constant,} &= \frac{K_1}{K_2} \\ &= \frac{4x^2}{(1-x)^2}. \end{aligned}$$

It is evident therefore that

(1) The equilibrium is independent of the volume, and therefore also of the pressure. (2) Increasing the proportion of Hydrogen or Iodine will tend to greater combination. (3) If the equilibrium constant K is known for any temperature, x can be calculated for that temperature, and the equilibrium composition ascertained.

Direct experiment has verified these conclusions. Thus, Lemoine, and Bodenstein and Meyer found that in increasing the pressure the rates of reaction in the system



were increased, but the equilibrium remained unchanged. Catalysts likewise increased the rates, without altering the final equilibrium. Addition of excess of either Hydrogen or Iodine increased the amount of combination.

Lemoine found that at 350°C . Hydriodic acid dissociated, and gave an equilibrium mixture in which 19 per cent. had changed to Hydrogen and Iodine. We will calculate from this (a) the equilibrium constant K for 350°C ., (b) the composition of the equilibrium when 2 volumes of Hydrogen are mixed with 1 volume of Iodine at 350°C .

If 19 per cent. of Hydriodic acid is dissociated at 350°C ., the composition of the gaseous mixture will be HI 81.0 per cent.; Hydrogen 9.5 per cent.; and Iodine 9.5 per cent. Therefore at volume V , the concentrations will be $\frac{81}{V}$, $\frac{9.5}{V}$, and $\frac{9.5}{V}$ respectively.

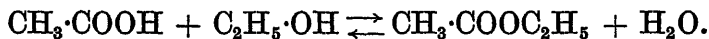
$$\begin{aligned} 2\text{HI} &\rightleftharpoons \text{H}_2 + \text{I}_2 \\ \therefore \left(\frac{81}{V}\right)^2 K &= \frac{9.5}{V} \times \frac{9.5}{V}. \\ \therefore K &= \left(\frac{9.5}{81}\right)^2 = 0.0137. \end{aligned}$$

If now 2 gram-molecules of Hydrogen are mixed with 1 gram-molecule of Iodine in a total volume V , and x gram-molecules of each undergo combination to Hydriodic acid, the respective concentrations will be $\frac{2-x}{V}$, $\frac{1-x}{V}$, and $\frac{2x}{V}$.

$$\therefore \left(\frac{2x}{V}\right)^2 K = \left(\frac{2-x}{V}\right)\left(\frac{1-x}{V}\right).$$

Substituting $K = 0.0137$, and solving for x , we obtain $x = 0.95$. The quantities of Hydrogen, Iodine, and Hydriodic acid in the equilibrium mixture will therefore be 1.05, 0.05, and 1.9 gram-molecules respectively.

2. Esterification of Acetic Acid with Ethyl Alcohol.



Suppose 1 gram-molecule each of Acetic acid and Alcohol are mixed and allowed to attain equilibrium. When the composition has become constant, suppose that x gram-molecules have undergone

change. The concentrations will then be Acetic acid $\frac{1-x}{V}$, Alcohol $\frac{1-x}{V}$, Ethyl acetate $\frac{x}{V}$, and water $\frac{x}{V}$.

$$\therefore \left(\frac{1-x}{V}\right)^2 K = \left(\frac{x}{V}\right)^2$$

or
$$K = \frac{x^2}{(1-x)^2}.$$

Direct experiment shows that when equimolecular quantities of Alcohol and Acetic acid are mixed, 66 per cent. undergoes esterification. In the above equation, x therefore = 0.66. Hence $K = \frac{(0.66)^2}{(0.33)^2} = 4$.

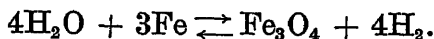
Berthelot and Pean de St. Gilles found that for this reaction, K was almost independent of the temperature. Knowing its value, we are able to calculate the composition of any equilibrium mixture: For example, 1 gram-molecule of Alcohol and 2 gram-molecules of Acetic acid will attain equilibrium when

$$4 = \frac{x^2}{(1-x)(2-x)}.$$

Solving for x , we obtain $x = 0.85$. Hence the equilibrium mixture will contain 0.85 gram-molecule of Ethyl acetate and water, 1.15 and 0.15 gram-molecules, respectively, of Acetic acid and Alcohol.

So far we have only considered the application of the law of mass action to homogeneous systems. It can also be applied to heterogeneous systems, as follows:—

1. Solid-Gas Equilibria. It is necessary to assume that the active mass of the solid is constant, an assumption which experience justifies. Reactions between solids are rare, and we may suppose that when a solid and gas interact the reaction is really a homogeneous one, in the gas phase, the solid participating by virtue of its vapour pressure, which therefore represents its active mass. This vapour pressure is often infinitesimal, but so long as excess of solid is present, it will be constant at constant temperature. As an example, we will consider the reversible reaction



The active masses of the Iron and Iron oxide are constant. Hence if $[\text{H}_2\text{O}]$ and $[\text{H}_2]$ represent the partial pressures of water vapour and Hydrogen in the equilibrium:—

$$\left(\frac{[\text{H}_2\text{O}]}{[\text{H}_2]}\right)^4 = \text{constant}.$$

Deville verified this relation, and Preuner (*Z. Phys. Chem.*, 1904, 47, 385) found for this ratio the following mean values :—

| | | | | | |
|---------|---|---|---|---|------|
| 900° C. | . | . | . | . | 0.69 |
| 1025 | . | . | . | . | 0.78 |
| 1150 | . | . | . | . | 0.86 |

2. Solid-Liquid Equilibria. Again the active mass of the solid may be assumed constant, an assumption justified by the fact that solids and liquids will probably interact in the liquid phase, and the solubility of the solid for a given temperature is constant.

3. Liquid-Gas Equilibria. The reaction may occur either in the liquid phase, due to solution of the gas, or in the vapour phase, owing to vaporisation of the liquid, or in both together. The active mass of one of the reactants will be constant in either of the simple cases.

Influence of Temperature on Equilibrium

To understand the effects of temperature on chemical change at one time occasioned considerable difficulty. Thus, it was noticed that whereas most dissociations were increased when the temperature was raised, the opposite was the case with Hydriodic acid and some few other compounds. In reversible reactions, elevation of temperature generally shifted the equilibrium, but the direction of displacement could not be predicted. These difficulties disappeared as soon as the idea of reaction velocity was recognised and the connection between reaction velocities and equilibria in reversible systems clearly understood. Thus, it was found that the reaction velocity of a chemical change is always increased by raising the temperature. The amount of this increase for a definite rise of temperature varies widely between different reactions, but it is generally considerable. This acceleration also takes place when the temperature of a reversible system is raised, the speeds of both forward and reverse actions being increased, though generally to different extents. The point of equilibrium is therefore shifted, and the displacement may be in either direction, according to whether the acceleration of speed is greater for the forward or the reverse change. In the few cases in which the equilibrium is not altered by a rise of temperature, the rates of both forward and backward changes are accelerated in an equal degree. A general principle, showing how all chemical and physical equilibria are influenced by changes of pressure, temperature, or concentration, was enunciated by Le Chatelier in 1884, and independently by von Braun in 1887-8. It may be stated as follows :—

“ If in any system in equilibrium one of the conditions (temperature, pressure, or concentration) governing equilibrium be altered,

the system will change, and in such a manner that the alteration of conditions to which it is subjected tends to be opposed," or:—

"A system in equilibrium is conservative, and tends to counteract any change. Alteration of temperature, pressure, or concentration will therefore shift the equilibrium, or change the system in such a way as partially to annul that alteration."

This principle has been described as "The Principle of Least Action" (Le Chatelier) and "The Law of Mobile Equilibrium" (Van 't Hoff). Although in the first instance it was founded on experience, it is contained in the second law of thermodynamics, as Van 't Hoff has shown. Since it depends on no hypotheses or assumptions in regard to the molecular structure of matter, it is valid for all equilibria, whether physical or chemical, thus:—

Water is in equilibrium with ice at 0° C. and 760 mm. pressure. If the pressure be raised, ice tends to melt. This is in accordance with the principle, since ice contracts in volume on melting, and this contraction partially annuls the increased pressure. Application of pressure therefore lowers the melting point of ice. The reverse is the case with most substances: they contract on solidification, and their melting points are therefore raised by pressure.

All solid substances melt on heating. This illustrates the principle, since all solids absorb heat in changing from the solid to the liquid state.

The principle would also lead us to expect that substances which dissolve in a solvent with absorption of heat will increase in solubility as the temperature is raised. Experience shows that this is true. Heat of solution is, in the great majority of cases, negative, and elevation of temperature therefore leads to increased solution, since it is by displacement of the equilibrium in this direction that the rise of temperature tends to be opposed. (*N.B.*—Combination between solute and solvent sometimes takes place, with evolution of heat, *e.g.*, heat of hydration, and this may mask the heat of solution.) Some substances dissolve in water with evolution of heat, *e.g.*, Gypsum, and Sodium sulphate at temperatures above its transition point. In accordance with the principle, these substances become less soluble in water as the temperature is raised.

In the reversible chemical reaction



we can deduce from Le Chatelier's rule: (1) Since the forward reaction is exothermic, rise of temperature will shift the equilibrium in the backward direction, that is, towards greater dissociation, while lower temperatures will favour the formation of Ammonia. (2) The forward reaction takes place with contraction of volume.

Increase of pressure will therefore favour it and shift the equilibrium towards the right.

Dissociation, in far the greater number of cases, occurs with absorption of heat. A temperature change will therefore evoke an alteration in the equilibrium which partly counteracts the change, that is, rising temperature will favour greater dissociation, and *vice versa*. For those compounds which dissociate with development of heat (see, for example, Hydriodic acid, below) the reverse is true.

The principle also shows that a reaction which takes place with increase of volume will tend to be suppressed by application of pressure. When no volume change accompanies a reaction, pressure will have no influence on the equilibrium, while reactions which take place with diminution of volume will be assisted by pressure.

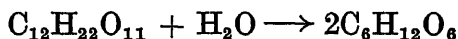
The heat of a chemical reaction generally varies with the temperature at which the reaction is carried out. The dissociation of Hydriodic acid is an extreme instance of this,



since below about 320° C. the dissociation is exothermic, while above this temperature heat is absorbed. In accordance with Le Chatelier's principle, we should therefore expect that below about 320° C. a rising temperature would favour combination of Hydrogen and Iodine, while above this temperature—the reverse, that is—dissociation of Hydriodic acid to Hydrogen and Iodine would be increased. Bodenstein confirmed these expectations as follows:—

| Temp. | Degree of dissociation. | | | |
|---------|-------------------------|---|---|--------|
| 290° C. | . | . | . | 0.1637 |
| 310 | . | . | . | 0.1669 |
| 320 | . | . | . | 0.1601 |
| 340 | . | . | . | 0.1706 |
| 350 | . | . | . | 0.1763 |
| 394 | . | . | . | 0.1957 |
| 444 | . | . | . | 0.2143 |

According to Röntgen and Rothmund, 100 atmospheres pressure increased the rate of inversion of cane-sugar by about 1 per cent. (*Z. Phys. Chem.*, 1896, 20, 168). It follows that the reaction



must take place with a small contraction of volume.

The principle of Le Chatelier and von Braun was investigated more exactly by Van 't Hoff, who deduced the expression

$$\frac{d \log_e K}{dT} = - \frac{U}{RT^2}$$

from the Laws of Thermodynamics (K is the equilibrium constant of the mass action law, T is the absolute temperature, U is the decrease of total internal energy occurring when the stoichiometric quantities in gram-molecules undergo reaction, and R is the gas constant per gram-molecule). If the reaction is carried out at constant volume, so that no heat is expended in external work, then, if Q is the heat of the forward reaction in a reversible system,

$$Q = U,$$

and the above equation becomes

$$\frac{d \log_e K}{dT} = - \frac{Q}{RT^2}.$$

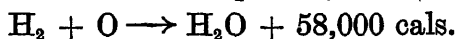
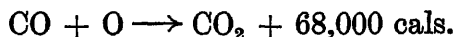
From this equation, the principle of Le Chatelier at once follows. Thus, if the forward reaction is exothermic, Q is positive, and $-\frac{Q}{RT^2}$ is therefore negative. For a temperature increment dT , the value of $\log_e K$ therefore diminishes. Hence, if the temperature of a system in equilibrium is raised, the backward (endothermic) reaction is accelerated more rapidly than the forward (exothermic), and the point of equilibrium is shifted in the direction which absorbs heat. Similarly, if the forward reaction is endothermic, Q is negative, and $-\frac{Q}{RT^2}$ is positive. The value of K therefore increases with temperature, so that the forward (endothermic) reaction is favoured.

The equation also enables us to calculate the displacement of the equilibrium in a reversible reaction, due to a given temperature change, if the thermal value of the reaction is known. Conversely, by measuring the equilibrium displacement caused by a definite temperature change, the heat of reaction at constant volume can be deduced. Thus, if K_1 and K_2 are the equilibrium constants at the absolute temperatures T_1 and T_2 , we obtain by integration

$$\log_e K_1 - \log_e K_2 = \frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right),$$

from which, if the equilibrium K_1 at T_1° Abs. is known, we can calculate the equilibrium K_2 at T_2° Abs., or, knowing both K_1 and K_2 , we can evaluate Q . Knowing the heat of reaction and the value of the equilibrium constant K for one particular temperature, we can therefore calculate the value of K for any temperature, and thence, by application of the mass action law, deduce the equilibrium composition. For example, we will calculate the composition of the water gas obtained when equal volumes of water vapour and Carbon monoxide, in presence of a catalyst, attain their equilibrium at

1200° Abs. Molecular heats of combustion are $H_2 = 58,000$ cals., and $CO = 68,000^\circ$ cals., or



Hence, by subtraction,



The reaction takes place without volume change, so that no heat is consumed or liberated on account of external work.

From the mass action law,

$$[CO][H_2O]K = [H_2][CO_2]$$

$$\therefore K = \frac{[H_2][CO_2]}{[CO][H_2O]}$$

By experimental determination of these concentrations, the equilibrium constant, K_1 , at 1000° Abs. has been found to be 3.26.

$$\text{We have } \log_e K_1 - \log_e K_2 = \frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

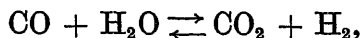
$$\therefore \log_{10} K_1 - \log_{10} K_2 = \frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \times 0.4343.$$

Substituting $T_1 = 1000^\circ$ Abs., $K_1 = 3.26$, $T_2 = 1200^\circ$ Abs.,

$$\log 3.26 - \log K_2 = \frac{10,000 \times 200 \times 0.4343}{1.985 \times 1000 \times 1200}.$$

$$\therefore \log K_2 = 0.149 \quad \therefore K_2 = 1.41.$$

If now, x is the fraction of water vapour or carbon monoxide transformed in the change



$1 - x$ will be the fraction remaining, and x will represent the quantities of Carbon dioxide and Hydrogen formed,

$$K = \frac{[H_2][CO_2]}{[CO][H_2O]}$$

$$1.41 = \frac{x^2}{(1-x)^2}$$

$$x = 0.542.$$

The composition of the water gas mixture at 1200° Abs. will therefore be

| | | | | |
|-----------------|---|---|---|-------|
| Carbon dioxide | . | . | . | 27.1% |
| Hydrogen | . | . | . | 27.1% |
| Water vapour | . | . | . | 22.9% |
| Carbon monoxide | . | . | . | 22.9% |

N.B.—The application of the equation

$$\frac{d \log_e K}{dT} = - \frac{Q}{RT^2}$$

assumes that Q is independent of the temperature. This is not strictly true, since the heat value of a reaction may alter considerably according to the temperature at which it is carried out. The results must therefore be regarded as approximate only. Also it is apparent that to determine K for any temperature, the value of K for some particular temperature must be known. These two deficiencies were made good by Nernst.

Experience has shown that the total energy change U in gaseous reactions at any temperature can be expressed as a function involving a series of ascending powers of T , the absolute temperature. Thus,

$$U = U_0 + \alpha T + \beta T^2 + \gamma T^3 + \dots \text{etc.},$$

where U_0 represents the hypothetical heat of reaction in the neighbourhood of 0° Abs. Substituting this value of U in the Van 't Hoff equation,

$$\frac{d \log_e K}{dT} = - \frac{U}{RT^2},$$

and integrating, we obtain

$$\log K = \frac{U_0}{RT} - \frac{\alpha}{R} \log T - \frac{\beta}{R} T - \frac{\gamma}{2R} T^2 \dots \text{etc.} + I,$$

where I is the integration constant.

If the value of the equilibrium constant for some one temperature is known (K_1 at T_1° Abs.) we can integrate between the two temperatures T_1 and T_2 , when I vanishes, as follows:—

$$\log K_1 - \log K = \frac{U}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right) - \frac{\alpha}{R} \left(\frac{\log T_1}{T} \right) - \frac{\beta}{R} (T_1 - T) \dots \text{etc.},$$

and the value of the equilibrium constant, corrected for variation of Q with temperature, can be determined for any temperature.

The great importance of Nernst's contribution is in the evaluation of the integration constant I , and in distinguishing the significance of the constants α , β , γ , etc., so that by application of Nernst's

theorem it becomes possible to determine K for any temperature, in any reversible reaction, providing only that certain heat constants are known.

It is impossible here to follow all the ultimate consequences of the application of Nernst's heat theorem to physico-chemical research. For this, the more recent editions of Nernst's work must be consulted, or Lewis' "Physical Chemistry," Volume II, or the original papers. It will be sufficient if we state certain of Nernst's formulæ, give an example of their application, and indicate their value in the study of chemical reactions, especially catalytic gas reaction.

After converting natural into ordinary logarithms, the most useful form of the Nernst Heat Equation is

$$\log K = \frac{Q_0}{4.571T} + \Sigma v \cdot 1.75 \log T - \frac{\beta}{4.571}T - \frac{\gamma}{9.14}T^2 + \Sigma vC.$$

Q , the heat of reaction at constant pressure, is related to Q_0 as follows:—

$$Q = Q_0 + \Sigma v \cdot 3.5T + \beta T + \gamma T^2,$$

while C represents the "chemical constant," which has been calculated for a number of substances. The most important are

| | | | | | |
|--------|-------|--------|-------|----------|-------|
| H_2 | = 1.6 | Cl_2 | = 3.1 | NH_3 | = 3.3 |
| N_2 | = 2.6 | HCl | = 3.0 | H_2O | = 3.6 |
| O_2 | = 2.8 | NO | = 3.5 | C_6H_6 | = 3.0 |
| CH_4 | = 2.5 | SO_2 | = 3.3 | | |
| CO | = 3.5 | CO_2 | = 3.2 | | |

The notation " ΣvC " implies that the sum of the constants corresponding with each molecular entity in the reaction must be taken. Thus, in the reaction



since the constants for Hydrogen, Oxygen, and water are 1.6, 2.8, and 3.6, respectively,

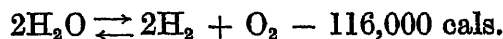
$$\begin{aligned}\Sigma vC &= 2 \times 1.6 + 2.8 - 2 \times 3.6 \\ &= -1.2\end{aligned}$$

since the constants β and γ are not always easy to obtain, and are small, the approximate equation

$$\log K = \frac{Q}{4.571T} + \Sigma v \cdot 1.75 \log T + \Sigma vC$$

is convenient for practical use. Q is the heat of reaction at ordinary temperatures, under constant pressure, and can therefore be taken directly from thermochemical tables, or calculated.

We will apply this equation to calculate K at 1300° Abs. in the equilibrium



We have found that $\Sigma vC = -1.2$.

$$\therefore \log K = -\frac{116,000}{4.571T} + 1.75 \log T - 1.2.$$

If $T = 1300^\circ$ Abs.

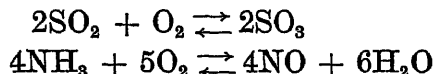
$$\begin{aligned} \log K &= -\frac{116,000}{4.571 \times 1300} + 1.75 \log 1300 - 1.2 \\ &= -19.53 + 5.45 - 1.2 \\ &= -15.3. \end{aligned}$$

This value is only approximate, but it shows that water is very little dissociated at 1300° Abs.

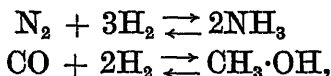
The practical importance of the results we have reached may now be indicated. Suppose we wish to prepare a substance, C , by the union of two gases, A and B , as follows:—



The Nernst theorem enables us to calculate the equilibrium constant for any temperature, with a sufficient approximation to show whether a practicable concentration of C , given a suitable catalyst, can be attained at any convenient temperature. Thus, the theorem shows that the reactions



are capable of realisation almost completely in the desired direction, and the choice of catalyst merely remains to be settled. The reactions



and

on the other hand, at all temperatures where interaction would seem at all reasonable, when examined by Nernst's method give value of K which show that, at ordinary pressure, the equilibrium mixtures only contain inappreciable quantities of Ammonia or Methyl alcohol. By taking this value of K , however, and applying the mass action law, it is found that K rises with increasing pressure, and that at 100 atmospheres, or above, the preparation of Ammonia or Methyl alcohol by these reactions is practicable. In yet other cases, calculation shows that K is small, even at high pressure. The reaction must then be regarded as unrealisable, and no catalyst can make any difference.

CHAPTER IV

THEORIES OF CATALYSIS

Liebig's Theory. Armstrong's Reversed Electrolysis. Chemical or Intermediate Compound Theories. Application to : (a) The Friedel-Crafts Reaction; (b) Hydrolysis; (c) The Benzoin Condensation; (d) Intramolecular Change of Chloro-amines. Adsorption Theory. Views of Faraday and of J. J. Thomson. Capillary Adsorption and True Adsorption. Langmuir's Theory. Adsorption and (a) Negative Catalysis; (b) Anticatalysis. Modifications of Langmuir's Theory. Adsorption and Catalysis in Solution. Activation Theories of Baly, Arrhenius. Lewis' Radiation Theory. Conclusion.

THE inceptions of the two older theories of catalysis, the chemical theory and the adsorption theory, have already been discussed. Liebig propounded a vibration theory (*Ann.*, 1839, 30, 241) on the mechanical analogy that vibrations are easily communicated to surrounding isochronous systems. He stated: "The cause of catalysis lies in the capacity which a substance undergoing decomposition or combination possesses of arousing in a body in contact with it the same chemical activity, or of making the body susceptible of the same kind of change." When he attempted to illustrate this perfectly rational but not very practical theory, Liebig involved himself in difficulties. He continued: "This capacity is best illustrated by a burning substance, by means of which similar activity is aroused in other bodies when we bring the burning one into contact with them." Criticism brought the following modification: "Just as heat is capable of disturbing the statical moment in the elements of many chemical compounds, so also can this be brought about by means of a substance of which the elements are themselves in a condition of disturbed equilibrium." Thus, in the fermentation of sugar, the "motion which the ferment atoms possess is imparted to the elements of sugar," which results in the resolution of the latter into simpler molecules.

A theory of "Reversed Electrolysis" was proposed by H. E. Armstrong to account for catalytic change (*B.A. Reports*, 1885, 1909; *J.C.S.*, 1903, 83, 1088). According to this idea, chemical reaction does not occur between two pure substances—a third is necessary. One of the components of a reacting system must be a conductor of electricity, and when the complex formed by the association of the reacting substances establishes a conducting

system, chemical change commences. The circuit of change is therefore analogous with a closed voltaic circuit, and until the catalyst completes such a system with the reactants, no change can take place. For example, Baker has shown that dry Hydrogen and Oxygen will not combine, and also that the trace of water formed when the mixture is raised to a red heat is not sufficient to determine explosion: in Armstrong's view, because the conductor is still lacking (Baker, *J.C.S.*, 1902, 81, 400). The theory of reversed electrolysis clearly implies that catalysis is universal, and that chemical change depends upon a transfer of electrical energy *via* the catalyst, between the reactants.

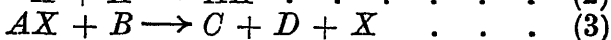
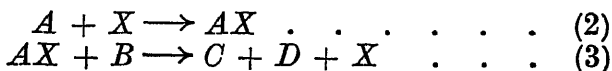
It is probable that no single theory is possible that will explain all types of reaction which it has become customary to class as catalytic. For reaction in homogeneous systems, the intermediate compound, or chemical theory, has gained very wide acceptance, and in most cases offers a complete picture of the reaction mechanism. It is also recognised that intermediate compound formation is by no means impossible in heterogeneous or contact catalyses, and many chemists have endeavoured to apply the theory universally. At the same time, it can be shown both on chemical and physical grounds that reaction must be aided powerfully by surface adsorption or condensation of the reactants. The evidence is convincing that this is an important factor, especially in "contact actions," and in those reactions in a liquid phase where absorption of a gas is aided by the presence of a finely-divided or colloidal solid. The influence of adsorption by no means rules out the formation of an intermediate compound at the same time, or of some form of intermediate complex between the adsorbed reactant and the adsorbing surface. Modern views are tending towards an explanation of catalysis on such lines (see Zalkind, *Z. Phys. Chem.*, 1923, 104, 77).

Chemical or Intermediate Compound Theories

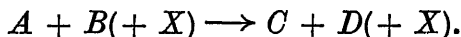
Intermediate compound theories all premise that catalytic reactions occur in stages. In the first stage one reactant combines with the catalyst, forming a labile intermediate compound. In a succeeding stage this labile complex reacts with another reactant, forming a new product, and regenerating the catalyst. Thus, the reaction



occurring in presence of a catalyst *X* will take place in a cycle of changes, the catalyst participating as follows:—



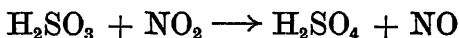
which on addition give



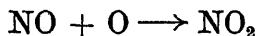
Since the rate of a reaction is determined by the rate of the slowest intermediate stage, it follows that in order that positive catalysis may occur, each change in the cycle must be faster than the direct reaction, that is, each of the reactions (2) and (3) above must be faster than (1). The conditions under which a sequence of reactions will be faster than a direct reaction leading to the same result are investigated theoretically by Herzfeld (*Z. Phys. Chem.*, 1921, 98, 161). It may be remarked that we have already found that reactions involving a number of molecules take place more easily in a series of mono- and di-molecular stages.

In many catalytic reactions the stages can be actually separated and carried out independently. The mechanism then is distinct, for example :—

1. The oxidation of Sulphurous to Sulphuric acid, using Nitric oxide as an oxygen carrier (Clément and Désormes, *Ann. Chim.*, 1806, 59, 329). The two stages

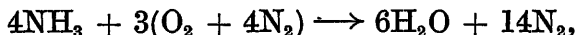


and

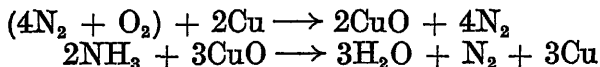


can be carried out either together or separately. When the two reactions are carried out together, another intermediate compound, Nitrosyl sulphuric acid, is frequently formed. Alternative intermediate courses besides the one formulated above have therefore been proposed to explain this oxidation. Which of these is the main one probably depends largely upon the condition of working.

2. Ammonia and air when passed over heated Copper or Copper oxide, produce Nitrogen and water :



but the reaction can equally well be conducted in two stages separately,



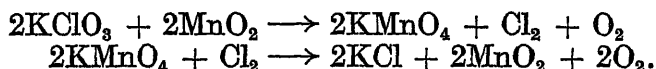
3. The Weldon Chlorine process similarly takes place in a series of cycles, the Manganese salts functioning as carriers of Oxygen from air to Hydrochloric acid.

4. When Anthracene is oxidised electrolytically in a Sulphuric acid bath, the oxidation is much facilitated by the presence of Cerium sulphate, or Chromic acid, especially the former. In the first stage of the process, the Ceric salt or Chromic acid oxidises

the Anthracene to Anthraquinone. The second stage consists in the electrolytic oxidation of the Cerous salt or Chromium sulphate back to the higher state of oxidation.

In other reactions the stages of the process cannot be isolated, but evidence is nevertheless convincing that intermediate products are formed, for example :—

1. The decomposition of Potassium chlorate in presence of Manganese peroxide. The intermediate formation of manganates and permanganates is established, since under certain conditions their characteristic colours can be obtained. The probable sequence of the reactions is

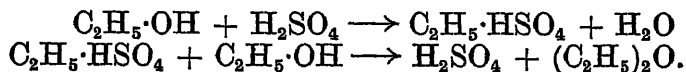


2. When Methyl alcohol is oxidised by air to Formaldehyde, in contact with a surface of metallic Copper at the lowest possible temperature, the surface of the latter undergoes a continuous change of colour and appearance. This is doubtless due to alternate oxidation and reduction of the metal (*N.B.*—the oxidation of Methyl alcohol takes place to a considerable degree in contact with almost any surface, *e.g.*, glass. Other factors besides intermediate compound formation are therefore involved here)..

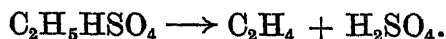
3. In the Haber Ammonia synthesis, powerful promoters for an Iron catalyst are metals which form nitrides under the conditions of working.

4. Hydrolyses in presence of acids and alkalies, the Deacon Chlorine process, and the Friedel-Crafts reaction have been exhaustively studied, and the formation of intermediate compounds, or complex ions, has been established.

5. The easy formation of Ethyl sulphuric acid from Alcohol and Sulphuric acid led Williamson, in 1850, to the view that formation of Ether involved the following stages :—



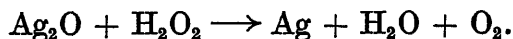
The dehydration of Alcohol, leading to Ethylene, probably takes a similar course :—



6. The specific action of enzymes would seem to be most easily explicable on the supposition that the enzyme attaches itself chemically to the molecules it attacks, and then exerts its characteristic action.

7. Bayley (*Phil. Mag.*, 1879, (5), 7, 126) has shown that Hydrogen peroxide oxidises the lower oxide of Cobalt, and that the peroxide

so formed then reacts with unchanged Hydrogen peroxide, both giving off Oxygen. The latter reaction is analogous to that between Silver oxide and Hydrogen peroxide,



This sequence of reactions explains the catalytic effect of Cobalt salts towards the decomposition of Hydrogen peroxide, and Bayley supposed that the catalytic decomposition of hypochlorites is effected in a similar manner, the Cobalt oxide oscillating between the compounds Co_3O_5 and CoO_2 . Hydrogen peroxide does not oxidise Nickel oxide to a peroxide, hence Nickel oxide does not catalyse its decomposition. If, however, Nickel peroxide is made independently, reaction between this and Hydrogen peroxide is rapid, both liberating their "peroxide oxygen."

In yet other cases, proof is completely lacking that intermediate compounds are formed during a catalytic reaction. This applies to most "contact" catalyses. The intermediate compound theory has nevertheless been very widely advocated even in these cases. Sabatier, from his researches on hydrogenation, concluded that Nickel exerted its action by virtue of an unstable hydride which alternately formed and parted with its Hydrogen. The oxidising catalytic action of Platinum has often been ascribed to alternate oxidation of the metal and reduction of the oxide. De la Rive (*Pogg. Ann.*, 1839, 46, 489), Brodie (*Phil. Trans.*, 1862, 151, 855), Engler and Wöhler (*Z. anorg. Chem.*, 1901, 21, 1), and Wöhler (*Ber.*, 1903, 584, 3475) all held this view, and the latter supposed that the active oxide was PtO . Later, Wöhler disproved this view by showing that PtO and PtO_2 were both less active than the metal in promoting the oxidation of Sulphur dioxide. As the action proceeded, however, these oxide catalysts increased in activity, until finally analysis showed that they had been completely reduced to metal (*Ber.*, 1906, 39, 3538; 1909, 42, 3326). It must therefore be concluded that the oxidising activity of Platinum in no wise depends upon the intermediate formation of a compound of the usual type between Platinum and Oxygen. It is now generally admitted that all the available evidence is against the formation of such compounds in contact actions, and in many other heterogeneous catalyses. Thus, hydrides of Nickel are almost certainly not formed when this metal is used as a hydrogenating catalyst, either in gaseous or liquid phase reactions, and Thoria or Alumina probably do not form compounds at a high temperature with substances whose dehydration they facilitate. In cases of heterogeneous catalysis, the evidence is clear that another type of chemical association—Adsorption—occurs between the surface atoms of the solid (the catalyst) and one or more of the reactants, and that this form of combination can be

as effective in promoting catalysis as the formation of the usual type of chemical compound. Indeed, according to modern views, there is no fundamental difference between a chemical compound as generally understood and the union between an adsorbed substance and the adsorbent. Both types of combination are due to operation of chemical forces (primary or contra-valencies), but whereas in the one case the compounds are easily shown to possess a fixed and invariable composition, in the other a continuous variability in composition between certain limits can be obtained. Stoichiometric relations are much more difficult to demonstrate in cases of adsorption, since they can only exist between the number of surface atoms of a solid and the number of atoms the surface adsorbs at saturation.

It is now believed that catalysis is always preceded by a chemical union, either in definite proportions or by adsorption, between the catalyst and one (or more) of the reactants. The formation of such a compound does not, of course, necessarily produce catalysis, since the addition of a third substance to a pair of reactants does not always aid their interaction, even when the third substance is capable of forming a labile complex with one of them. Likewise a body may be a powerful adsorbent, and yet weak, or even completely inert as a catalyst. The conditions under which catalysis will follow are entirely unknown, notwithstanding the supreme importance of the question. The chief difficulty in catalytic research—the discovery of a suitable catalyst—would be at once overcome if it were possible to elucidate the conditions under which an intermediate chemical association is formed and leads to catalysis.

The mechanism of catalysis therefore involves a union between the catalyst and one or more of the reacting substances, the resulting compound being either definite in composition or apparently indefinite, and formed by adsorption. In either case, the reaction must occur in stages. The details of these stages are generally unknown, and their elucidation constitutes the second of the major unsolved problems of catalysis. In homogeneous catalytic systems, various intermediate stages have sometimes been distinguished, and intermediate compounds isolated and formulated. In "contact" systems almost nothing is known regarding the stages of a catalytic reaction—how, for example, the molecules of Alcohol and Ammonia first attach themselves to a dehydrating catalyst and then are resolved into amine and water. The recent researches of Harkins and of Langmuir on orientated adsorption may eventually lead to a fuller understanding of the stages a compound passes when it is first adsorbed and then undergoes chemical change.

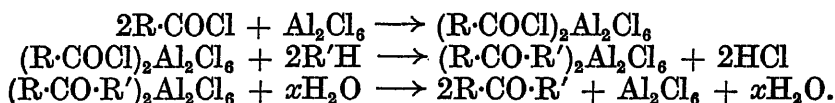
In homogeneous systems the possibility of adsorption does not occur, and the only intermediate compounds that can be formed are

of the type defined by Proust, many years ago, possessing definite and invariable compositions. We shall now review the evidence which has in many cases established the formation of such compounds in catalytic changes.

The Friedel-Crafts Reaction

In the synthesis of aromatic hydrocarbons and ketones, as well as many other reactions in which anhydrous Aluminium or Ferric chlorides are used as catalysts, the formation of intermediate compounds is clearly proved.

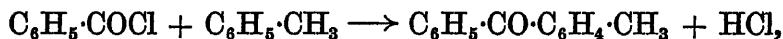
Perrier (*Ber.*, 1900, 33, 815) and Böeseken (*Rec. trav. chim.*, 1900, 19, 19; 1901, 20, 102) isolated crystalline double compounds of Aluminium chloride with acid chlorides and ketones, corresponding with the general formulæ $(R \cdot COCl)_2Al_2Cl_6$ and $(R \cdot CO \cdot R')_2Al_2Cl_6$. They therefore suggested that the ketone synthesis, using an aromatic hydrocarbon and an acid chloride, occurred in the following stages:—



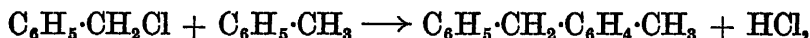
Kronberg (*J. pr. Chem.*, 1900, II, 61, 494) attempted to assign constitutional formulæ to these compounds, and Kohler (*Amer. Chem. J.*, 1900, 24, 385) obtained the molecular weights of some of the corresponding Aluminium bromide compounds, and found that they corresponded with the formulæ given.

Gustavson (*Chem. Centr.*, 1883, 14, 344) obtained compounds from Aluminium bromide and Benzene or Toluene, and Konowalov and Plotnikov (*J. Russ. Phys. Soc.*, 1899, 31, 1020) described a whole series of such compounds. Gustavin (*C.R.*, 1903, 136, 1065; 1905, 140, 940) isolated a number of compounds of the type $Al_2Cl_6 \cdot C_6H_6$. Finally, Nencki (*Ber.*, 1899, 32, 2414) showed that anhydrous Ferric chloride also formed compounds.

In an elaborate dynamical study of the reactions between Benzoyl chloride and Toluene,



and Benzyl chloride and Toluene,



in presence of either Aluminium or Ferric chloride, Steele (*J.C.S.*, 1903, 83, 1470) adduced strong evidence in favour of the mechanism proposed by Perrier and Böeseken. In the first place, he pointed out that this mechanism explains why most reactions involving the use of Aluminium chloride as catalyst require a proportion commensurate with the other reactants, while in a few cases, particularly

when Ferric chloride is used, a relatively small quantity suffices, and the action is typically catalytic. The difference is owing to the combination of the catalyst with the product of reaction. When the compound so formed is stable, the catalyst is continuously withdrawn from the reaction, so that for the reaction to proceed to completion an amount of catalyst at least equivalent to the amount of the product is necessary. When no combination between the catalyst and product takes place, or when the compound formed is easily dissociable, then minimal amounts of Aluminium or Ferric chloride suffice.

Steele carried out the two reactions in excess of Toluene as solvent, and measured their progress by determining the rate of evolution of Hydrochloric acid.

Ketone Synthesis. In excess of Toluene, Steele anticipated that the rate would correspond with that of a monomolecular reaction. It was actually found, however, to depend on the proportion of Aluminium chloride used.

Using an amount of Aluminium chloride approximately equivalent to the Benzoyl chloride, the following results were obtained. After a short period of induction, the amount of Hydrochloric acid evolved was proportional to the time, and directly this ceased to be the case the reaction became monomolecular. These results admit of simple interpretation in accordance with the views of Perrier and Böesecken. The Aluminium chloride and Benzoyl chloride combine rapidly to form the complex $(C_6H_5 \cdot COCl)_2 Al_2 Cl_6$, whose solubility in Toluene is limited. Until the reaction mixture has become saturated with respect to this substance the rate of reaction is irregular. As soon as the solution is saturated the concentrations of the two substances $(C_6H_5 \cdot COCl)_2 Al_2 Cl_6$ and Toluene become constant, and therefore the rate of interaction between them becomes constant and the rate of evolution of Hydrochloric acid steady, that is

$$- \frac{dc}{dt} = K.$$

The reaction proceeds in this way until the complex $(C_6H_5 \cdot COCl)_2 Al_2 Cl_6$ is all dissolved, when its concentration commences to fall. The reaction then becomes monomolecular until it is completed, that is,

$$- \frac{dc}{dt} = Kc.$$

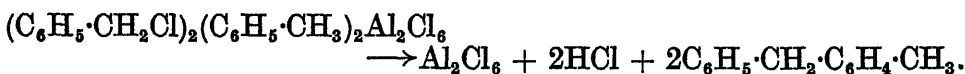
During the whole progress of the reaction, Aluminium chloride is withdrawn from the reaction in the form of a compound, $(C_6H_5 \cdot CO \cdot C_6H_4 \cdot CH_3)_2 Al_2 Cl_6$, with the product, which is stable under the conditions of the experiment.

When the ratio of Aluminium chloride to Benzoyl chloride is raised to 2.3 to 1, Steele found that after a short period of induction the reaction constant approximated to that required for a dimolecular reaction, that is,

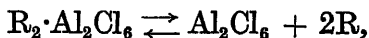
$$-\frac{dc}{dt} = Kc^2.$$

This indicates that Aluminium chloride combines with both the Benzoyl chloride and Toluene, and that reaction then occurs between the two complexes $(C_6H_5 \cdot COCl)_2Al_2Cl_6$ and $(C_6H_5 \cdot CH_3)_2Al_2Cl_6$.

Hydrocarbon Synthesis. Using widely varying proportions of Aluminium chloride, the reaction was monomolecular. After a short period of induction it proceeded in this way until for every gram-molecule of Aluminium chloride used 25 gram-molecules of Hydrochloric acid were liberated. The reaction then ceased. Evolution of Hydrochloric acid did not commence until an intense orange colour had developed in the reaction mixture, and this colour almost disappeared as the evolution came to an end. The colour was probably due to the presence of the complex compound $(C_6H_5 \cdot CH_2Cl)_2Al_2Cl_6$. The interpretation of the quantitative results is as follows: The complex $(C_6H_5 \cdot CH_2Cl)_2Al_2Cl_6$ forms rapidly, and the reaction as measured by the evolution of Hydrochloric acid is the rate of the decomposition,



The cessation of the reaction at a certain definite point is to be expected if we premise the formation of a dissociable compound between Aluminium chloride and the product. If this is represented by $R_2 \cdot Al_2Cl_6$, then the dissociation will be



and equilibrium will be established when

$$\frac{[Al_2Cl_6][R]^2}{[R_2 \cdot Al_2Cl_6]} = \text{constant}.$$

Hence as $[R]$ is increased, a value for $[Al_2Cl_6]$ will ultimately be reached which, for practical purposes, is zero. The Aluminium chloride will then exert no further effect, and reaction will stop.

Using Ferric chloride in the hydrocarbon synthesis, Steele could detect no evidence of formation of a compound with the product. The reaction then became truly catalytic.

Steele concluded that the function of Aluminium or Ferric

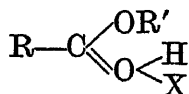
chloride in the Friedel-Crafts reaction was truly catalytic, and that the ketone and hydrocarbon syntheses were exactly analogous, differing only in the greater instability of the final complex in the case of the hydrocarbon.

Steele's conclusions have been confirmed by Goldschmidt and Larsen (*Z. Phys. Chem.*, 1904, 48, 430), who showed that the condensation of Benzyl chloride with Anisole was monomolecular and that the function of the Aluminium chloride was purely catalytic.

Hydrolysis

Hydrolytic actions are generally catalysed by acids or alkalis, that is, by Hydrogen or Hydroxyl ions. Strong evidence of the existence of stages and intermediate complexes (either molecules or ions) is afforded by the work of Kendall, Acree, and others.

The freezing points were determined of mixtures of (a) Dimethyl pyrone with monobasic acids, and phenols. (b) A carboxylic acid with a second acid, which may be either inorganic, another carboxylic acid, or a strong phenol. (c) Trichloroacetic acid with aldehydes and ketones. (d) Phenols with organic acids, or strong phenols. (e) Esters with acids, either inorganic or organic. Kendall showed in this way that combination occurred, and formulated the products as oxonium compounds, addition occurring at the Oxygen atom, which thereby became tetravalent. For example, the compound between an ester $R\cdot COOR'$ and an acid HX was represented



(*J. Am. C.S.*, 1914, 36, 1232, 1722; 1915, 37, 149; 1916, 38, 1309, 1712). The tendency to oxonium compound formation depends much upon the relative strengths of the acids used. Thus, a carboxylic acid with another acid yields an addition compound most readily when the strengths of the two acids are widely different. In such cases, the compound is generally easy to isolate in a pure crystalline condition of definite melting point. Acids of approximately equal strengths show less tendency to combine (note that glacial Acetic acid is dimolecular). Similar results are obtained with phenols, which are found to combine with strong phenols or strong acids, but not with other weak phenols. Combination likewise is most marked between strong acids and esters of weak ones. Among others, the following compounds were isolated: Ethyl acetate-Trichloroacetic acid (m. p. $-27.5^{\circ}C.$); Benzyl benzoate-Trichloroacetic acid (m. p. $11.9^{\circ}C.$); Ethyl oxalate-2-Trichloroacetic acid (m. p. $3.4^{\circ}C.$).

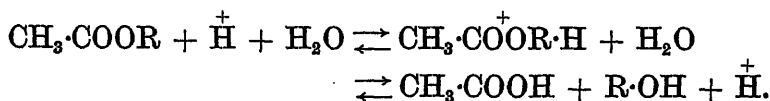
Even Acetic acid, when mixed with esters, was shown by the freezing-point curve to give appreciable oxonium formation.

In the last paper of the series, Kendall suggested that the formation of the oxonium compounds accounted for the catalytic action of acids in ester hydrolysis. Such labile addition compounds may be expected to form between two substances generally when one of them contains an atom possessing residual affinity. If the energy changes are conducive, the formation of these labile intermediate compounds will lead to catalysis.

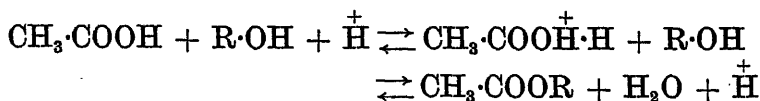
Many investigators have concluded that hydrolytic reactions, and others which are influenced catalytically by Hydrogen, Hydroxyl, or other ions, take place through the intermediate formation of complex ions. Thus Acree and his co-workers have investigated a number of reactions which are facilitated by acids and alkalies, such as:—

- (a) The formation and hydrolysis of esters.
- (b) The hydrolysis of amides.
- (c) The inversion of cane-sugar.
- (d) The action between Carbonyl compounds and Hydroxylamine, or Phenyl hydrazine.
- (e) The molecular rearrangement of Acetyl chloro(or bromo)-amino-benzenes (*Amer. Chem. J.*, 1907, 37, 410; 38, 258, 489; 1908, 39, 300, 1755; 1909, 41, 457).

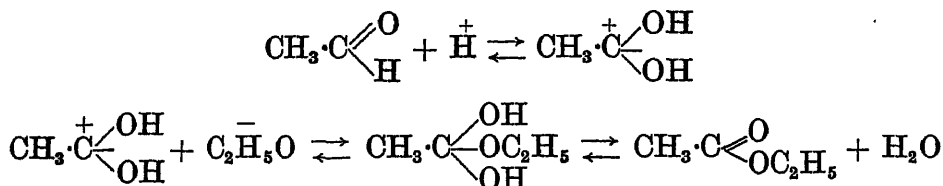
They found that the rates of certain of these reactions, calculated on the assumption of the formation of an intermediate complex ion agreed well with the observed values obtained by direct experiment. They therefore concluded that a combination between the compound undergoing hydrolysis and the ion catalysing the change was the first stage in the mechanism of the reaction. The work of Kendall already described, as well as the earlier researches of Baeyer and Villiger (*Ber.*, 1901, 34, 2679) and of Walden (*Ber.*, 1901, 34, 4185) show that divalent oxygen compounds possess basic properties which enable them to form addition products with strong acids. Hence divalent Oxygen compounds may be expected to form oxonium ions, by combination with acids, in the same way that Ammonia forms ammonium ions. Acree supposed that the hydrolysis of an ester proceeded as follows:—



Esterification of an acid was similarly represented:—

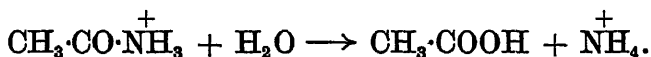


Lapworth suggested a configuration for the intermediate ion, and wrote the esterification as follows:—



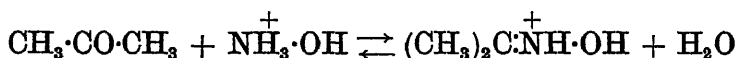
This, however, does not represent the complex ion as an oxonium ion, which, on the basis of Kendall's results and the analogy with "ammonium," "phosphonium," "sulphonium," etc., would seem more probable. Lapworth's view also assumes the Alcohol to ionise, which is at variance with Acree's results, although it is in agreement with the views expressed by Zengelis (*Ber.*, 1901, 34, 198) and by Euler (*Z. Phys. Chem.*, 1901, 33, 405, 641; 1902, 40, 498; 1904, 47, 353; *Ber.*, 1900, 33, 3202). Euler goes to the length of declaring that all reactions are really ionic, even though the degree of ionisation may be very small.

Acree and Nirdlinger found that the velocity of hydrolysis of Acetamide with Hydrochloric acid was consistent with the view that Hydrogen ions first united with the feebly basic Acetamide to form Acetamide cations, $\text{CH}_3 \cdot \text{CO} \cdot \text{NH}_3^+$, which then hydrolysed, with formation of Acetic acid and Ammonium ions:—

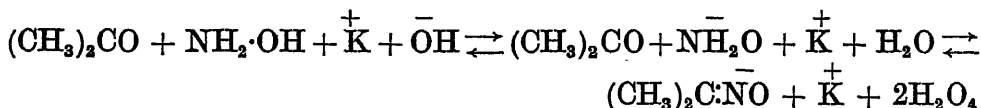


(See also Remsen and Reid, *Amer. Chem. J.*, 1899, 21, 281; Reid, *Amer. Chem. J.*, 1900, 24, 397.)

The reaction between Acetone and Hydroxylamine was found by Acree to be catalysed by both acids and alkalies. He formulated the reactions as follows:—



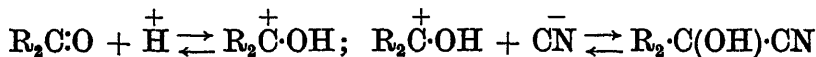
with acids, and with alkalies



which represent the catalysing acid or alkali as first forming a complex, either with the Hydroxylamine or the Acetone.

The Benzoin Condensation

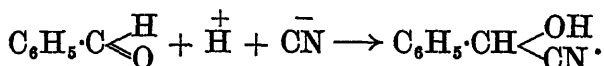
Definite evidence has been obtained that this reaction, catalysed by cyanide ions, occurs in stages. Lapworth (*J.C.S.*, 1903, 83, 995) proved that the addition of Hydrocyanic acid to aldehydes and ketones was much retarded by acids (Hydrogen ions), and therefore facilitated by the presence of bases or metallic cyanides which suppress the concentration of Hydrogen ions. He adduced evidence in support of the view that addition of Hydrocyanic acid to carbonyl compounds occurred with the ions, in one of the following ways:—



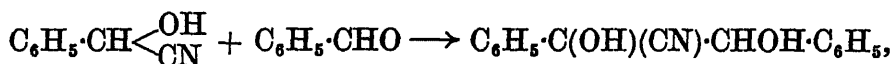
or



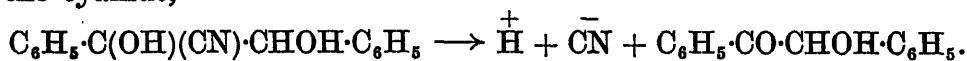
The Benzoin condensation, in presence of a cyanide as catalyst, was then explained as follows: Benzaldehyde and Potassium cyanide first produce Mandelonitrile,



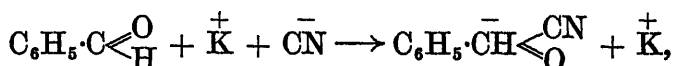
This possesses a reactive Hydrogen atom, and in alkaline solution condenses with another molecule of Benzaldehyde,



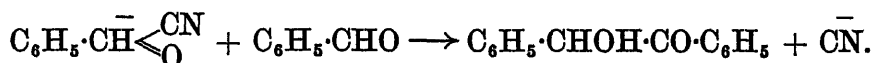
to give the unstable cyanhydrin of Benzoin, which at once regenerates the cyanide,



In accordance with the views first expressed, this sequence of changes may be formulated



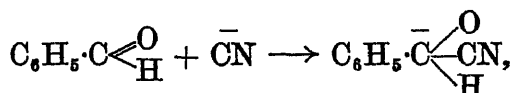
the complex ion so formed then reacting with another molecule of Benzaldehyde to give Benzoin,



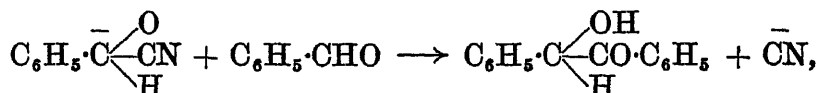
Bredig and Stern (*Z. Phys. Chem.*, 1905, 50, 513) found that the Benzoin condensation,



in presence of the cyanides of Sodium, Potassium, or Barium, was dimolecular, and that the velocity constant depended upon the concentration of the CN ion. They represented the mechanism as follows:—



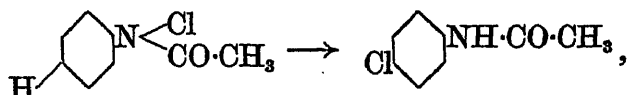
a very rapid reaction, and



which is slow, and is the reaction actually measured. This view is supported by the fact that the electrical conductivity of cyanide solutions is reduced by the addition of Benzaldehyde, which suggests the formation of a less ionised compound.

The Rearrangement of Phenyl Chloro-amines

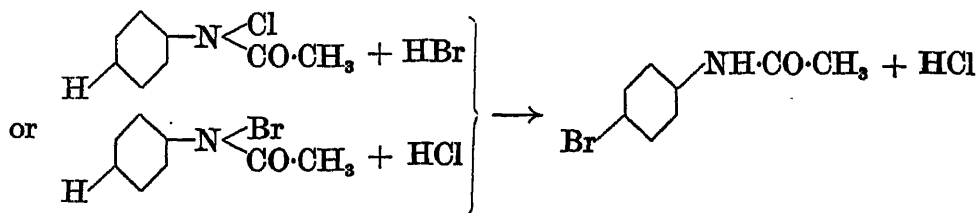
Blanksma (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 5, 178) showed that the velocity of rearrangement of Acetyl phenyl chloro-amine into para-Chloroacetanilide,



in presence of Hydrochloric acid was that of a monomolecular reaction, and that doubling the strength of the catalysing acid quadrupled the rate of reaction.

Acree and Johnson (*Amer. Chem. J.*, 1907, 37, 410; 1909, 41, 457) confirmed this observation, and showed that it is true also for the intramolecular rearrangement of the corresponding Acetyl phenyl bromo-amine into para-Bromo-acetanilide in presence of Hydrochloric acid. They inferred that the actual reacting substances were two complex ions formed by the union of the chloro- (or bromo-) amine with the ions of the Hydrochloric acid.

Acree and Johnson further found that Acetyl phenyl chloro-amine when treated with Hydrobromic acid, gave the same product as Acetyl phenyl bromo-amine, and Hydrochloric acid—namely, para-Bromoacetanilide in both cases.



It is impossible to resist the conclusion that the catalysing acid (or, as Acree supposed, its ions), first forms an addition compound with the chloro- or bromo-amine. The addition products in the two cases are identical, and the final product is para-Bromoacet-anilide, and not the chloro-compound, because the Bromine migrates much more rapidly than the Chlorine.

Adsorption Theory

The powerful influence that adsorption must possess in aiding chemical change was first recognised by Faraday (see Chapter I). He expressed the view that the catalytic action of Platinum in causing combination between Hydrogen and Oxygen was due to a condensation or concentration of the gases on the Platinum surface, and argued that these conditions would lead to increased reaction, both on account of the greater frequency of molecular impacts, and also because the act of adsorption would diminish the forces that oppose combination. Faraday's remarkable observations that Carbon monoxide and Carbon disulphide temporarily inhibited and Sulphuretted hydrogen and Hydrochloric acid permanently destroyed the catalytic activity of Platinum in inducing reaction between Hydrogen and Oxygen have already been mentioned. The idea of selective adsorption followed, and accounted for the phenomena of selective or fractional combustion observed by Henry (*Ann. of Philosophy*, 1825, 25, 422) and by Turner (*Edin. Phil. J.*, 1824, 11, 99, 311). Referring to the inhibiting action of foreign substances, Faraday wrote: "Whether the effect produced by such small quantities of certain gases depends upon any direct action which they may exert upon the particles of Oxygen and Hydrogen, by which the latter are rendered less inclined to combine, or whether it depends upon their modifying the action of the plate temporarily (for they produce no real change in it) by investing it through the agency of a stronger attraction than that of the Hydrogen—remains to be decided by more extended experiments.

"The very power which causes combination of Oxygen and Hydrogen is competent, under the usual casual exposure of Platina, to condense extraneous matters upon its surface, which take away its power of combining Hydrogen and Oxygen by preventing their contact with it."

Faraday's views were given more precise form by J. J. Thomson, in his "Application of Dynamics to Physics and Chemistry." From Laplace's theory of capillarity, Thomson deduced that chemical combination would occur more readily between liquids in thin layers, such as an adsorption layer, than in liquids in mass. Chemical actions which, it is claimed, can only be explained in this way have been observed by J. J. Thomson, and also by Liebreich (*Phil. Mag.*,

1887, 23, 468; 1890, 29, 216), by Liveing (*Proc. Camb. Phil. Soc.*, 1883, 14, 370), and by Bredig (*Z. Phys. Chem.*, 1899, 31, 258).

We shall see when discussing Langmuir's researches that the forces maintaining adsorption are probably the same as those of cohesion in solids, and "internal pressure," due to molecular attraction, in liquids. The magnitude of these forces is known to be enormous; thus, calculated from the latent heat of vaporisation, the internal pressure in liquid water exceeds 10,000 atmospheres. From the intensity of the forces involved, the tenacity with which adsorbed substances are held to the adsorbing surface can be well understood. A unimolecular adsorption layer of Oxygen on Platinum was found by Langmuir to be stable *in vacuo* up to 300° C. To remove the hygroscopic film from a glass surface requires a high vacuum, together with a temperature of not less than 300–400° C. Langmuir, however, considers that in this case solution phenomena as well as adsorption are involved, since the quantity of water in a hygroscopic layer on glass is much greater than that which corresponds with a covering of one layer of molecules. The power of capillary forces was shown by Mitscherlich, who found that when Carbon dioxide was adsorbed in wood charcoal at 1 atmosphere pressure and 12° C., it occupied only 1.7 per cent. of its original volume, and calculated from this that at the adsorbing surface at least one-third of the carbon dioxide must have been compressed into the liquid state.

The physical condition of adsorbed substances has been variously pictured by different investigators. In the case of charcoal and Carbon dioxide, the conception of a liquid or a highly compressed gas is probably justified. In those cases which Langmuir described as true adsorption there is evidence of an ordered orientation of adsorbed atoms or molecules, one layer thick, upon the adsorbing surface. It is clear that in either of these cases the conditions within the adsorption layer will be very different from the conditions of the same gas out of range of the adsorbing surface. Bancroft (*J. Phys. Chem.*, 1917, 21, 580; 1918, 22, 433) and J. J. Thomson ("Application of Dynamics to Physics and Chemistry," 1888, 203, 234) have shown that within an adsorption film the conditions are so altered that the position of a chemical equilibrium cannot be the same as in the free gas or vapour. An equilibrium displaced in this way cannot easily be detected experimentally, on account of the difficulty of removing a reaction product sufficiently rapidly from the influence of the adsorbing surface. Reid, however, has passed equimolecular volumes of Acetic acid and Alcohol over Silica gel at 100° C. and for a long period obtained yields of 76 per cent. of Ethyl acetate, notwithstanding that the equilibrium mixture at this temperature contains only 67 per cent.

Adsorption or condensation upon a surface may be of two kinds, (a) due to capillarity, or (b) true adsorption.

Adsorption due to Capillarity

When a liquid is enclosed in a capillary space so that its surface is concave, it exerts a lower vapour pressure than an open surface of the same liquid, at the same temperature. Thus, consider a capillary column, AB (Fig. 1), in a space which has been evacuated so as to contain only the saturated vapour of the liquid at a given temperature. The pressure at level A must be the same inside the capillary as outside, but less than the pressure at level B by an amount equal to the pressure of a column, AB , of saturated vapour. This being so, within very fine capillaries, such as the spaces of a highly porous solid, the vapour pressure of a substance may be so much reduced that, even considerably above its normal boiling point, liquid within the capillaries is in equilibrium with gas outside. The action of porous substances, such as charcoal, is of this nature, gases or vapours being condensed as a result of capillary forces, and passing by adsorption into the liquid state. When adsorption is due to this cause, the amount bears a relation to the ease of liquefaction of the adsorbed gas.

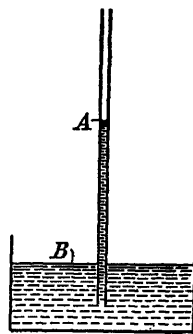
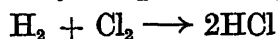
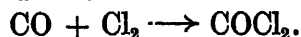


FIG. 1.

The phenomena of contact catalysis, and the numerous theories that have been advanced to account for them on the basis of adsorption, have been fully discussed by Bancroft (*J. Phys. Chem.*, 1917, 21, 573, and many papers since). He concluded that contact catalysis depended upon adsorption, and that sometimes it could be entirely explained on the basis of increased surface concentration. Thus, when two gases which are capable of slow reaction are brought into contact with a highly porous solid such as charcoal, if adsorption occurs, this will increase their concentrations, and augment the rate of interaction accordingly. For example, Bancroft predicted that Silica gel would catalyse the esterification of Acetic acid with Alcohol at 100°C ., since this reaction was known to occur in the vapour state in the absence of a catalyst (*Trans. Am. Electrochem. Soc.*, 1920, 37, 31). This has been verified by Reid. In the presence of porous charcoal, Hydrogen and Chlorine unite rapidly and smoothly, even in the dark and at the ordinary temperature, giving Hydrochloric acid,



and Carbon monoxide and Chlorine under the same conditions give Carbonyl chloride (phosgene),

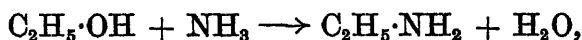


Much heat is evolved, so that the catalyst requires strong cooling in both reactions. Charcoal similarly brings about the oxidation of Alcohol vapour in presence of air, giving Acetic acid (Calvert, *J.C.S.*, 1867, 20, 293).

Clearly in all these cases intermediate formation of oxide or chloride of Carbon is out of the question, and since the action consists simply in speeding up reactions which proceed slowly in the absence of a catalyst, increased concentration of the gases due to adsorption is a natural explanation. In most cases, however, as Bancroft recognised, increased surface concentration is not sufficient to account for all the facts observed. Thus, Hydrogen and Oxygen when mixed and compressed to 2000 atmospheres are stable, yet contact with metallic Platinum, even at the ordinary temperature and pressure, at once determines their union. Charcoal, which also adsorbs Hydrogen and Oxygen, has a comparatively feeble catalytic effect. A specific surface effect, due probably to surface chemical affinities, is therefore apparent when reactions are induced by true adsorption, and this effect is frequently of greater importance than increased concentration. This point is illustrated by many observations. For example, Silica gel is a powerful adsorbent, and catalyses the reactions



and



but it does not as a rule catalyse the same reactions as either Platinum or charcoal (Taylor, *Trans. Am. Electrochem. Soc.*, 1919, 36, 150). Nickel is one of the most powerful hydrogenating catalysts, but some other metals adsorb Hydrogen with considerably greater avidity. Kramer and Reid (*J. Am. C.S.*, 1921, 43, 882) found that when Thorium nitrate is heated very suddenly by dropping into a red-hot crucible, the Thoria formed is especially light, porous, and bulky, 7 grams occupying 200 c.c. of space. They were surprised to find that this very porous material is almost inert for certain reactions in which Thoria prepared by other methods is a satisfactory catalyst.

Specific catalytic effects are generally most noticeable where catalysis is accompanied by true adsorption.

True Adsorption

Condensation due to capillarity is not described as "adsorption" by Langmuir, this term being restricted to those cases where surfaces by virtue of unsaturated chemical affinities combine with atoms or molecules with which they are in contact. This union

between surface molecules may occur at any interface between two phases, gaseous, liquid, or solid. In cases of true adsorption between a gas and a solid surface, the degree of adsorption bears no relation to the ease of liquefaction of the gas, being simply dependent upon the specific properties of the surface and the gas in question. It is mostly in these cases that specific catalytic action of a surface is manifested. When condensation is effected by capillarity, specific surface catalytic action may exist, but often it does not, reaction velocities being augmented simply on account of the increased concentrations of the reacting substances. True adsorption, on the other hand, is closely connected with catalysis in contact actions and in reactions in liquid media where a finely-divided catalyst in suspension is employed, being the determining influence in positive catalysis, negative catalysis, and anticatalysis. Thus, the effect of surface combination, or adsorption, like the formation of intermediate compounds in homogeneous systems, may be conducive, or otherwise, to chemical reaction, and positive or negative catalysis result, or if a surface possesses a stronger affinity for a foreign body than for a reactant, the former will be adsorbed to the exclusion of the latter, and the foreign body will act as a poison towards the reaction in question.

In 1914, Langmuir commenced the study of adsorption and related physico-chemical phenomena, and a remarkable series of papers followed. They are collated in *Transactions of the Faraday Society*, 1922, 17, 607, 621. ✓

In the first place he reviewed the work of Sir W. H. and W. L. Bragg on crystal structure, and the relation of their practical results to the theories of chemical constitution put forward by Werner, Stark, J. J. Thomson, and Lewis. He concluded that intermolecular forces cannot be divided into physical and chemical, since all are essentially similar and of the same nature as those implied by the term "Valency."

Until Langmuir developed his theory it was generally supposed that at a bounding surface between a liquid and its vapour, or between a solid and a gas, there was a continuous gradation between the two phases. Van der Waals considered that between the liquid and its vapour a layer existed in which the density and other properties passed gradually from those of the liquid to those of the vapour. Eucken (*Verh. deut. Physik. Ges.*, 1914, 16, 345) believed that the layers of gas in contact with a solid surface resembled a miniature atmosphere, the molecules being subject to an attractive force due to the presence of a solid. Backen (*Z. Phys. Chem.*, 1915, 89, 1) accounted for surface tension in a similar way.

The theory of Langmuir differs from these views in supposing an abrupt transition in passing through the surface of a solid or a

liquid. The surface atoms of either must be regarded as held to the underlying atoms by the same forces that bind the atoms within the mass; but while the forces within the mass are symmetrically disposed and balance one another, conditions at the surface are asymmetric, and a field of force directed outwards must be expected to operate. Surface atoms are therefore "unsaturated," since they possess a residual attractive force not satisfied by any form of combination with adjacent atoms. Various considerations, especially the work of Bragg, lead to the view that such forces are of the same nature as ordinary chemical valencies, either principal or secondary, and these according to Langmuir are responsible for all surface phenomena, the forces maintaining adsorption, surface tension, cohesion, viscosity, and controlling evaporation, condensation, solution, and crystallisation, being all chemical, and exhibiting in consequence the wide variations of intensity characteristic of valency forces. Adsorption of the so-called permanent gases by solids generally involves only secondary or residual valencies, but many cases of adsorption, especially by metals, are due to primary valencies.

If this view of surface affinity is correct, then the atoms or molecules composing a sharp edge, or point, of a solid should possess greater unsatisfied affinity, and therefore greater chemical reactivity than the atoms or molecules at a flat surface. Reboul (*C.R.*, 1913, 155, 1227; 156, 548) and Reboul and Luce (*C.R.*, 1921, 172, 917) show, in fact, that the rate of chemical action at surfaces is greatest at the points of greatest curvature.

Langmuir showed that all previous quantitative work on adsorption was invalidated by the following factors. (a) Employment of porous solids as adsorbers, which precluded any accurate reckoning of the surface exposed. (b) Solution, or absorption, was not distinguished from adsorption. (c) Use of gases or vapours approaching the saturation limit made it possible for condensation of liquid to occur in considerable quantities, especially in capillary spaces.

From theoretical considerations it was deduced that the surfaces of solids and liquids are inelastic to collision of gaseous molecules. When a gas molecule impinges upon a surface it therefore does not rebound, but coalesces, or condenses, being held by the surface field of force. These condensed molecules eventually evaporate, and the time that elapses between condensation and evaporation depends on the strength of the surface force. The adsorption layer is the direct result of this condensation, so that if the surface forces are intense—as, for example, between principal valencies—evaporation will be slow, and the surface will become more or less covered with a layer of molecules. When the surface forces are weak, evaporation occurs soon after condensation, and only a small part of the surface is covered. The adsorbed layer is generally not more

than one molecule deep, since as soon as the surface is completely covered the surface forces are chemically saturated, and the range of these forces (of the order of 10^{-8} cm.) is less than the diameter of a molecule.

✓ Langmuir has produced striking confirmation of his theory (*J. Am. C.S.*, 1916, 38, 2221; 1917, 39, 1848). For the quantitative results, the original papers must be consulted. Layers were found to be only one molecule deep in all cases of true adsorption, such as condensation of gaseous molecules on solid surfaces, floating films of oils on liquids, and adsorbed layers of dissolved substances on immersed surfaces. When the surface was saturated, the adsorbed layer consisted of a single layer of tightly-packed molecules, regularly orientated, as would be expected on the theory. This regular orientation had already been inferred in the case of films of oil on water from the experiments of Rayleigh, Marcelin (*Ann. Physik*, 1914, 1, 19), Devaux, and especially of Harkins (*J. Am. C.S.*, 1917, 39, 354, 541). According to Harkins, at the interface between water and another liquid the molecules at the surface of the latter set themselves in such a way as to turn their most active, or polar group (e.g., $\cdot\text{COOH}$, $\cdot\text{COOC}_2\text{H}_5$, $\cdot\text{CN}$, etc.) towards the water. Langmuir's results indicate that in unimolecular films of fatty acids on the surface of water the molecules are so arranged that the carboxyl groups (which possess more residual affinity than the hydrocarbon chains) are united to the surface water molecules by primary or secondary valencies, while the hydrocarbon chains are crowded into the space above.

These views had been anticipated as far back as 1888 by Debus, and used by him to explain the catalytic decomposition of Hydrogen peroxide (*J.C.S.*, 1888, 53, 327). When two molecules collide "in the position of reaction," decomposition into water and Oxygen results, while if they encounter in any other aspect, decomposition does not occur. Hence substances will either promote or retard the decomposition of Hydrogen peroxide according to their "polarising" effect on the molecule. Platinum promotes decomposition by causing the molecules so to arrange themselves that an Oxygen atom is turned towards the Platinum. This has the effect of bringing Oxygen atoms of different molecules into close proximity and arranging for their more frequent encounter in the "position of reaction."

Since adsorption is accompanied by a definite orientation of the adsorbed molecules, then if the orientation is not conducive to reaction, negative catalysis, as implied by Debus, might be expected to follow. Instances of this have recently been discovered by Kruyt and Van Duin (*Rec. trav. chim.*, 1921, (4), 2, 249), who have shown that the following reactions are retarded by charcoal, although

the reacting substances are adsorbed: Saponification of Ethyl acetate, and of Methyl benzoate para-sodium sulphonate. Addition of Bromine to the acid Sodium salt of para-Sulpho cinnamic acid. Removal of Bromine from the neutral, and acid Sodium salts of para-Sulphodibromohydrocinnamic acid by Potassium iodide. On the other hand, the removal of Bromine from $\alpha\beta$ -Dibromopropionic acid by Potassium iodide is accelerated by adsorption in charcoal.

These cases of negative catalysis are easily explicable on the basis of orientated adsorption. Thus, if two substances are restrained in their movements, either by adsorption or any other influence, encounters will be less frequent, and interaction therefore slower. Or, if the adsorbed substance is attached to the adsorbing surface by the reactive grouping, this is not so easily available for reaction. Again, at a surface between water and Carbon, we have seen that adsorbed molecules are directed with their more polar groupings towards the water. If the reaction occurs at a non-polar or less polar portion of the molecule, this part is therefore turned away from the water and the substances which are dissolved in it. For example, in the case of Ethyl acetate, the C:O group is the most polar, and the :O will consequently extrude into the water, while the $\cdot\text{O}\cdot\text{C}_2\text{H}_5$ group will be buried in the charcoal, where it is less accessible to the saponifying agent. A lower reaction velocity must therefore result. When two reactants are adsorbed, this may tend either to keep apart, or bring together, the reactive groupings, and negative or positive catalysis follow accordingly.

✓ In a third paper (*J. Am. C.S.*, 1918, 40, 1361), Langmuir completely developed the theory of adsorption on plane surfaces. The faces of crystals are known to consist of atoms, forming a regular lattice pattern, this resembling a checker board. When molecules of a gas are adsorbed by such a surface, they take up definite positions with respect to the surface lattice, and thus tend to form a new lattice above the old. On account of this regular orientation of molecules on an adsorbing surface, stoichiometric relations might be expected to hold between quantities of different adsorbed substances. Definite relations have, in fact, been found in the case of unimolecular films of various fatty acids in water. When a gas is adsorbed on a solid surface, however, other considerations enter. Thus, the adsorbed molecules may be too large for the elementary spaces available for them to occupy. The consequent overcrowding is analogous to the phenomenon of steric hindrance, and stoichiometric relations generally fail to hold, on account of a deficiency of adsorbed molecules.

Langmuir strongly emphasises that adsorption is a chemical process. Whereas earlier workers who favoured a chemical theory of adsorption believed that definite chemical compounds were formed

on the surface, Langmuir supposes the adsorbed atoms to be united by chemical forces with the surface atoms of the solid (or liquid), these in turn being similarly united to those below them, and so on throughout the whole mass. "Although the forces involved in the formation of such adsorbed layers are not different from those in the formation of chemical compounds, yet the chemist has not devised any terminology for such types of chemical combination, and, therefore, often fails to realise the similarity between these phenomena and those typical chemical phenomena to which his language applies more directly."

Experiments described in this paper on the adsorption of common gases by mica, glass, and Platinum surfaces illustrate the application of Langmuir's theory to catalysis. At ordinary temperatures, and pressures of about 0.1 mm. of Mercury, adsorption by glass and mica was negligible, less than 1 per cent. of the surface being covered by a single layer of molecules. At -183°C. , relatively large amounts of all gases except Hydrogen were adsorbed. At somewhat higher pressures, the surface tended to become saturated, but the maximum quantities adsorbed, even with saturated surfaces, were somewhat below the amounts expected for a unimolecular layer. The amounts of the different gases adsorbed by saturated surfaces of mica and glass were always in the order Hydrogen, Oxygen, Argon, Nitrogen, Carbon monoxide, Methane, and Carbon dioxide, and the adsorption was easily and quickly reversible.

In the case of adsorption on a Platinum surface, strikingly different results were obtained. Even at -183°C. , no adsorption occurred at first. After heating the metal to 300°C. in a mixture of Hydrogen and Oxygen at low pressure, however, the metal became "activated," and it then not only adsorbed Oxygen, Hydrogen, and Carbon monoxide, but also rapidly catalysed their union. The maximum quantities of Oxygen and Carbon monoxide adsorbed corresponded with unimolecular layers, and they could not be removed by pumping or heating. The forces holding these gases in union with the Platinum are therefore supposed to be of the primary valence type. Even at 300°C. , the Carbon monoxide could only be partially removed by pumping, and the Oxygen was even more firmly held. When excess of Oxygen was present, the amount adsorbed by the Platinum increased as the temperature was raised. The action was not reversible.

When Oxygen was brought into contact with Platinum containing adsorbed Carbon monoxide, or when Carbon monoxide was introduced to Oxygen adsorbed in the same way, union of the two gases occurred rapidly, and the Carbon dioxide formed showed relatively little tendency to remain adsorbed. In the same way, "activated" Platinum rapidly catalysed the union of mixtures of Hydrogen and

Oxygen, or of Carbon monoxide and Oxygen. The connection between adsorption and catalytic action is here very clearly established. The chemical activity of a solid surface was stated by Langmuir to depend on (1) the nature, (2) the arrangement, and (3) the spacing of the atoms forming the surface layer.

A systematic study of the adsorption of Hydrogen, Carbon monoxide, Carbon dioxide, and Ethylene by the hydrogenating metal catalysts, viz., finely-divided Nickel, Cobalt, Iron, Copper, Palladium, and Platinum, has been undertaken by Taylor and Burns (*J. Am. C.S.*, 1921, 43, 1273) and by Taylor and Gauger (*J. Am. C.S.*, 1923, 45, 920), while the adsorption of Carbon monoxide, Carbon dioxide, Oxygen, Hydrogen, and Nitrogen by oxide catalysts, viz., Copper oxide, Manganese peroxide, Cobalt sesquioxide, Ferric oxide, Vanadium pentoxide, and Silica, has been investigated at various temperatures by Benton (*J. Am. C.S.*, 1923, 45, 887, 900). Their results establish the influence of adsorption both on catalysis and anticatalysis.

Nickel subjected to varying heat treatment was shown to exhibit different capacities and rates of adsorption of Hydrogen, and the catalytic activity of the metal varied in close correspondence. Metals reduced from their oxides at a low temperature adsorbed Hydrogen much more strongly than when the reduction was carried out at a high temperature. Ever since Sabatier and Senderens discovered catalytic hydrogenation it has been known that the activity of finely-divided metals varies with their temperatures of reduction in the same way.

Benton found the same relation between adsorption, catalysis, and anticatalysis in the case of the oxides. The adsorbing power of Copper oxide depended much upon its mode of preparation, and its catalytic activity varied in exactly the same way. Oxides made by precipitation of the hydroxide, and drying at 150–200° C., adsorbed large quantities of Carbon monoxide and dioxide, but comparatively little Nitrogen, Oxygen, or Hydrogen. This agrees with the fact that precipitated oxides are powerful catalysts for the oxidation of Carbon monoxide, and also burn this gas selectively in mixtures of Carbon monoxide, Hydrogen, and air. Certain mixtures of oxides are so effective in these respects that it is possible to oxidise Carbon monoxide completely at 0° C., while mixtures of oxides can also be prepared which will cause the combination of Carbon monoxide and Oxygen under conditions where Hydrogen is completely unaffected, providing a basis for the analysis of mixtures containing these gases.

Modifications of the Langmuir conception of adsorption and catalysis have been proposed by Taylor, as a result of hydrogenation investigations, using a Nickel catalyst (*Proc. R.S.*, 1925, A, 108, ✓

105). X-Ray examination showed that metallic catalysts generally possessed the definite space-lattice structure of the crystalline metal, but groups of surface atoms existed in which the crystallisation process was incomplete. Taylor regarded the surface as composed of atoms saturated to varying degrees by neighbouring metal atoms. Supposing in the case of Nickel that four constraints exist for each atom, resembling those which attach the CO groups in Nickel carbonyl, then the degrees of unsaturation, or the number of free linkings of surface Nickel atoms, will vary between 1 and 3, according to the number which are unsatisfied by underlying atoms. In certain circumstances, it would therefore appear that both components of a hydrogenation reaction may attach themselves to the same Nickel atom. Points at which this occurs are supposed by Armstrong and Hilditch to correspond with the active catalytic patches which they believe to be present on a catalytic Nickel surface (*Trans. Faraday Soc.*, 1922, 17, 670; *Proc. R.S.*, 1925, A, 108, 111).

Armstrong and Hilditch proposed a still more definite form for the "adsorption complex." They suggested that the attraction between an unsaturated organic compound and an unsaturated Nickel atom (as pictured by Taylor) may be so great that the latter may be momentarily detached from its neighbours as catalytic action occurs. For a moment, there may then exist, apart from the solid surface, a complex of Nickel, unsaturated substance, and Hydrogen: an intermediate compound which then resolves itself into the product of reaction, regenerating the Nickel.

Adsorption and Catalysis in Solution. The adsorption theory is also applicable to heterogeneous catalyses in liquid media, when the catalyst is a finely-divided or colloidal solid, or an enzyme. When a solid is added to a solution, the concentration of the solute may be increased by adsorption at the solid surface. Chemical reaction may therefore be augmented, and its rate will depend upon the rate of diffusion of the reactants to the particles of catalyst, through the products of reaction. When the catalyst is sufficiently finely divided, its brownian movement may assist the process of diffusion.

The adsorption theory of catalysis for heterogeneous reactions in liquid media has received strong support from the researches of Armstrong, on the rate of hydrolysis of Lactose by the enzyme Lactase (*Proc. R.S.*, 1904, 73, 508). He found that in concentrated solution, using small quantities of Lactase, the quantity of Lactose hydrolysed per unit of time was always the same, and independent of the concentration so long as this was great.

| Concentration of Lactose (per cent.). | Per cent. Hydrolysed (46 hours). | Weight Hydrolysed (46 hours). |
|--|-------------------------------------|----------------------------------|
| 10 | 22.2 | 2.22 |
| 20 | 10.9 | 2.18 |
| 30 | 7.7 | 2.21 |

In dilute solution, however, or when the enzyme was present in quantities comparable with the amount of Lactose, then the law of mass action was followed, and the quantity of Lactose hydrolysed per unit of time was proportional to its concentration.

| Initial Concentration (per cent.). | Lactose Hydrolysed (3 hours) (per cent.). | Velocity Constant (Monomolecular). |
|---------------------------------------|--|---------------------------------------|
| 1 | 18.5 | 0.03 |
| 0.5 | 18.6 | 0.03 |
| 0.2 | 20.8 | 0.034 |

The explanation of these results is as follows: As the concentration of Lactose in solution increases, the adsorbed concentration also increases, and so long as the solution is very dilute, the two concentrations increase approximately proportionally. While this is the case, the reaction will follow the law of mass action, its rate being proportional to the concentration in the adsorbed layer. As the concentration of Lactose increases, the concentration in the adsorbed layer will still rise, but less rapidly. The velocity constant will therefore tend to fall. As the concentration of the Lactose is increased still further, the colloid particles ultimately become saturated, or completely covered with an adsorbed layer. Beyond a certain point, therefore, increasing the concentration of the solute does not alter the concentration adsorbed. The amount changed per unit of time then becomes constant.

Similar results were obtained by Bredig and Von Berneck in the decomposition of Hydrogen peroxide by colloidal Platinum. They found that the reaction was not strictly monomolecular, since (as in the case of Lactose above) the velocity constant rose as the Hydrogen peroxide was used up, due to the adsorbed Hydrogen peroxide decreasing in concentration relatively less rapidly than that in solution.

Adsorption and Anticatalysis

All theories of heterogeneous catalysis agree in supposing that catalytic action is localised at the surface of the catalyst. Any influence that reduces the frequency or effectiveness of contacts between reacting molecules and a catalytic surface will therefore be anticatalytic. It can be shown that any hindering of access to the surface of a catalyst will exert a disproportionately large effect in lowering the velocity of reaction (Bancroft, *J. Phys. Chem.*, 1917, 21, 734; Taylor, *Trans. Am. Electrochem. Soc.*, 1919, 36, 149).

Faraday was the first to show that traces of grease or other substances soiling the surface of Platinum rendered it catalytically inert. Berliner showed that the traces of grease from the atmosphere, or from stopcocks lubricated with grease, were sufficient to prevent

altogether the adsorption of Hydrogen by Palladium (*Wied. Ann.*, 1888, 35, 903). Schönbein (*J. pr. Chem.*, 1843, 29, 238), investigating the combustion of Hydrogen and Ether with air in presence of a Platinum catalyst, observed that the action of the Platinum was retarded or stopped by the presence of small quantities of the Hydrides of Sulphur, Selenium, Tellurium, Phosphorus, Arsenic, or Antimony, and supposed that their influence was due to the deposition of a film of the element upon the metal. We now know that these gases themselves are strongly adsorbed by Platinum, and that decomposition into their elements is not necessary to account for the formation of a covering film over the metal.

A reduced reaction velocity was first attributed to decreased adsorption by Bodenstein and Fink (*Z. Phys. Chem.*, 1907, 60, 61). The development of the idea is largely due to Langmuir, who has described some remarkable results (*J. Am. C.S.*, 1915, 37, 1163). Thus, substances which are strongly adsorbed displace others for which the surface affinity is less. A strongly-adsorbed gas, which may be the resultant of a reaction, will therefore more or less cover the surface of a catalysing solid, and poison it with respect to all reactions in which the reacting substances are less strongly adsorbed.

A pressure of 10^{-9} atmosphere of Oxygen was shown to lower enormously the emission of electrons from a Tungsten filament at 1500°C . Also when a Tungsten filament at 1200°C . was exposed to a mixture of Oxygen and Hydrogen at low pressure, the Oxygen united exclusively with the Tungsten to form Tungstic oxide, which vaporised from the filament. As soon as the Oxygen had all united with the Tungsten, the electron emission from the filament increased, and simultaneously the Hydrogen began to react, first dissociating into atoms in contact with the Tungsten, and then reacting with the Tungstic oxide. Langmuir concluded from these results that even at 1200°C ., and very low pressure, the Tungsten was covered with a stable adsorbed layer of Oxygen which impeded the emission of electrons and prevented the formation of atomic Hydrogen which normally happens under these conditions. As soon as all the Oxygen had been consumed by adsorption, followed by union with Tungsten to form the volatile oxide, the normal properties of the Tungsten surface were able to reassert themselves. The action of Oxygen in hindering emission of electrons and preventing dissociation of Hydrogen is entirely analogous to that of a catalytic poison, and it can hardly be doubted that it is due to adsorption, by which the active surface of the metal is covered with a stable film of adsorbed Oxygen.

The same poisoning effect of Oxygen was found when a filament was heated in mixtures of Carbon monoxide and Oxygen, or Methane and Oxygen. Tungstic oxide was formed as before, as though no

Carbon monoxide or Methane was present. When Methane alone, at low pressure, was used, the hot filament gradually decomposed it into Hydrogen and Carbon, the latter forming a solid solution with the Tungsten, from which it could be burnt by admission of Oxygen.

Ammonia at low pressures, in contact with a Tungsten filament at 750°C ., was decomposed rapidly into Nitrogen and Hydrogen unless a small amount of Oxygen was present, in which case the decomposition did not occur even at 900°C . At somewhat higher temperatures than this, action between the Tungsten and Oxygen commenced, giving Tungstic oxide, the Ammonia, like the Hydrogen, Carbon monoxide, and Methane in the previous experiments, being quite unaffected.

When a mixture of Oxygen and Cyanogen was exposed to the action of a Tungsten filament at 1250°C ., the metal did not oxidise until all the Cyanogen had first been burnt to Carbon monoxide and Nitrogen. Tungstic oxide then commenced to form. The Cyanogen would therefore appear to form a more stable surface combination than Oxygen with Tungsten: that is, Cyanogen must be a more powerful catalytic poison for Tungsten than Oxygen. Langmuir showed that this was also the case with Platinum: thus, at 350°C ., Carbon monoxide and Oxygen combined readily in presence of Platinum, while at 650°C ., even at low pressure, the reaction was very fast *unless Cyanogen was present*, in which case no reaction at all occurred. By slightly raising the temperature, the Cyanogen was oxidised to Carbon monoxide and Nitrogen, and as soon as all the Cyanogen had been consumed the activity of the Platinum was restored.

The systematic investigations of Taylor and Burns (*J. Am. C.S.*, 1921, 43, 1273), of Taylor and Gauger (*J. Am. C.S.*, 1923, 45, 920), and of Benton (*J. Am. C.S.*, 1923, 45, 887, 900), to which we have already referred, show conclusively that where catalysis is the result of true adsorption then a foreign body will act as a poison when the catalysing surface possesses a stronger affinity for the foreign body than for the reactants. Thus, it is well known that Platinum catalyses reactions of Carbon monoxide (*e.g.*, its union with Oxygen), while towards certain other reactions in which Platinum is the catalyst Carbon monoxide acts as a poison [*e.g.*, the combination of Hydrogen and Oxygen and the hydrogenation of Ethylene (Lunge and Harbeck, *Z. angew. Chem.*, 1896, 16, 50)]. Taylor and Burns clearly associate these observations with the fact that, even at pressures of Carbon monoxide not exceeding a few centimetres, a Platinum surface is so completely covered with an adsorbed layer of Carbon monoxide that Hydrogen and other gases cannot obtain access to it. In the same connection, they pointed out that Platinum, owing to its powerful attraction for Carbon monoxide, is a bad catalyst for the reduction of Carbon monoxide to Methane, while Palladium, from which

adsorbed Carbon monoxide is readily displaced by the stronger affinity which Palladium has for Hydrogen, is a good catalyst. Oxide catalysts which promote the union of Carbon monoxide and Oxygen at ordinary temperatures are highly porous, and as a consequence of capillary action very hygroscopic. Therefore, as would be expected, these catalysts are quickly poisoned by traces of free water vapour when used at the ordinary temperature and their activity is restored by drying. Only adsorbed water exerts a deleterious action, since the catalysts themselves contain water of hydration, chemically combined, which can only be driven off completely by heating to a very high temperature.

Carbon dioxide is powerfully adsorbed by dry precipitated oxides, and exerts a distinct anticatalytic influence. One of the most active catalysts for the oxidation of Carbon monoxide is a mixture of Manganese peroxide (60 per cent.) and Cupric oxide (40 per cent.), which induces rapid action at 0°C ., while either individual constituent requires a much higher temperature. The mixture is actually found to adsorb Carbon dioxide, the product of reaction, much more weakly than either Copper oxide or Manganese peroxide alone.

Carbon monoxide is well known to constitute a powerful poison for a Nickel catalyst in hydrogenation processes below 180°C . Above this temperature, Nickel and Carbon monoxide have no affinity for one another (or the latter is reduced to Methane), and anticatalytic action disappears.

Researches by Maxted also lead to the conclusion that catalytic poisoning is due to adsorption (*J.C.S.*, 1919, 115, 1050; 1920, 117, 1280, 1501; 1921, 119, 225, 1280). Poisons for a Platinum or a Palladium catalyst in hydrogenation reactions were shown always to lower the adsorption of Hydrogen. Thus, Hydrogen sulphide which is strongly adsorbed by Platinum, is a powerful poison for a Platinum catalyst. On heating Platinum containing adsorbed Hydrogen sulphide, the latter is decomposed catalytically, evolving an equivalent volume of Hydrogen, and the resulting sulphurised Platinum, although powerfully poisoned by the presence of the Sulphur, is not so completely inert as originally.

Maxted also made quantitative measurements of both the adsorptive power and catalytic activity of Platinum and Palladium containing varying small proportions of each of the following inhibitants: Lead, Mercury, Sulphur, Arsenic, and Zinc. In each case the catalytic activity was a linear function of the percentage of anti-catalyst present, that is, the degree of inhibition varied directly with the proportion of inhibitant up to the point at which inhibition was practically complete. One milligram of Lead was found to paralyse 8.8 milligrams of Platinum.

In the cases where adsorptive power was measured for varying proportions of inhibitor, the relation again was shown to be linear, that is, the adsorptive power varied inversely as the percentage of inhibitor. The coefficients of "inhibition of catalytic activity" and "inhibition of adsorption power" were not, however, equal. Thus, while 0.17 gram-atom of Lead per gram of Palladium reduced its adsorption power by one-half, only 0.02 gram-atom was required to reduce the catalytic activity by the same amount. Maxted explained this by supposing that the catalytic activity of Palladium was confined to the surface of the metal, while the occlusion of Hydrogen was not. Moreover, the poisoning coefficient for catalytic activity varied according to the mode of preparation of the catalyst and its fineness of division, while the coefficient for inhibition of adsorption power did not vary in the same way.

The effects of Carbon monoxide on Palladium had already been studied by de Hemptinne (*Z. Phys. Chem.*, 1898, 27, 249), who showed that Palladium treated with Carbon monoxide lost its power of occluding Hydrogen, at any rate at low temperatures, while Paal and Hartmann (*Ber.*, 1910, 43, 243) found that Carbon monoxide retarded its catalytic action towards Hydrogen and Sodium picrate. More recently, Paal and Hartmann (*Ber.*, 1918, 51, 711) and Paal and Steger (*Ber.*, 1918, 51, 1743), studying the poisoning of colloidal Platinum by Mercury, have shown that the latter is able to displace adsorbed Hydrogen from Platinosols.

Activation

Many theories, mostly too vague to be useful, have been put forward from time to time to account for catalysis on the basis of intermediate compound formation and adsorption. These generally consist of ingenious suggestions to account for reacting molecules becoming "activated," or brought into a condition more prone to react by the presence of the catalyst.

If we consider a chemical reaction from the standpoint of the kinetic theory, and assume that every impact between two reacting molecules leads to reaction between them, then clearly there is no room for catalysis, since by no possible means can the number of these impacts be increased except by increasing the speed of molecular movements, that is, by adding energy. If, however, only a certain proportion of collisions result in reaction, then any influence which renders a collision more fruitful, that is, activates the molecules in such a way that a greater proportion lead to reaction, then catalysis will follow.

Strutt concluded that molecules of Ozone react every time they encounter molecules of Silver oxide. Here, then, there can be no catalysis. Molecules of active Nitrogen, however, make on an

average 500 impacts with Copper oxide for each pair of molecules reacting (*Proc. R.S.*, 1912, 87, A, 302). Langmuir found that 15 per cent. of all Oxygen molecules at a pressure not greater than 5 bars, which strike a Tungsten filament at 2500° C., react with it to form Tungstic oxide. This coefficient increases as the temperature rises, and at 3000° C. about 50 per cent. of impacts produce Tungstic oxide. The effect that different solvents produce on the velocity of a reaction would seem very likely to be due to some influence of the solvent rendering a greater or less proportion of molecular impacts productive of reaction.

If we accept Langmuir's view of orientated adsorption, then, as Bancroft has pointed out, the possibilities become numerous. For example, on this view all the molecules are turned the same way. This may mean that all are directed so that at each molecular encounter the reactive groupings are the parts of the molecules to make contact. This would lead to positive catalysis, while if the orientation were adverse to molecules meeting in the "positive of reaction," then negative catalysis would follow (see Debus, *J.C.S.*, 1888, 53, 327). Activation on this idea would consist in a directive influence of the catalyst, helping molecules to meet in the position of reaction. Moreover, when a substance is adsorbed on different surfaces, the attachment may be to different groups. Thus, according to Sabatier, Methyl acetate decomposes in three distinct ways, according to whether Nickel, Thoria, or Titania is used as a catalyst. Bancroft has suggested that the attachment between Methyl acetate and the catalyst may depend on different groupings in the several cases, when bombardment of the captive (adsorbed) molecules by free ones would lead to different results in the three cases.

Other suggestions to account for activation have been put forward. An old idea of Loew (*J. pr. Chem.*, 1875, 11, 372) attributed catalytic action to the sharp irregularities of the catalyst surface, which broke down the molecules striking it into atoms, thus rendering them reactive. Bodenstein considered that when Hydrogen molecules are adsorbed on a Platinum surface they are deformed, and possibly broken down into atoms, these being held to the surface by electronic forces between the free atom and an atom of the metal. Raschig (*Z. angew. Chem.*, 1906, 19, 1748, 2083) considered that the forces peculiar to an adsorbing surface changed the forms of the adsorbed particles. This change might consist in a disruption of the molecules into atoms, or a displacement of parts of a molecule relative to one another, without breaking the molecular structure, thereby raising their potential energies. Alternatively, the vibrations of atoms and atomic groupings within the molecule may be altered, increasing in amplitude in the same way as when the temperature is raised. In this sense, the rise of reaction velocity with temperature may be

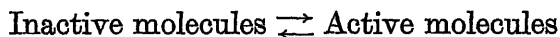
classed as catalytic. Light likewise can function as a catalyst, as, for example, in causing Carbon monoxide and Chlorine to unite. This action, Raschig concluded, could only be explained by supposing the light to exercise some action on the interacting molecules, perhaps splitting the Chlorine into atoms. If this be so, then, it was argued, the material catalysts should function in the same way as the non-material (heat and light), and increase the activity of reacting molecules by altering their form, or possibly by cleaving them into atoms.

In this connection, reference may be made to the rather vague "Dislocation Theory" proposed by Böeseken (*Rec. trav. chim.*, 1910, 29, 85; 1911, 30, 381; 1920, 39, 622).

Baly and Krulla have suggested that a partial conversion of one or more reacting substances into active forms may occur through a rupture of principal valencies or contravalencies, opening up fields of force around the molecule (*J.C.S.*, 1912, 101, 1469). Their idea is as follows: Principal and secondary valencies are possessed by all atoms, and when atoms unite, a residue of secondary valencies in general results. To this must be added any unsaturation of the principal valencies, so that a field of force will surround or radiate from each atom. Lines of force of opposite polarity within a molecule will tend to neutralise one another, with decrease of free energy—resulting in a lower reactivity of the atom or molecule concerned. Any influence that tends to open these closed lines of force will therefore increase reactivity. The function of a catalyst may therefore be to unlock, or open, in some way the condensed system of force lines within a molecule (Baly and Rice, *J.C.S.*, 1912, 101, 1475). For example, Baker has shown that when Ammonia and Hydrochloric acid, or quick lime and Carbon dioxide, are quite pure and dry, they do not react with one another. This is because the force lines are so completely neutralised within the molecules that there is insufficient residual affinity in either molecule to start a reaction. Water opens these closed systems of lines of force, and since it is not consumed in so doing, a small quantity induces the combination of unlimited quantities of either of the above pairs of substances. Similarly, Ammonium chloride, when pure and dry, does not dissociate when vaporised, because heat alone cannot open the fields of affinity within the molecule. Baly's theory can equally well be applied to negative catalysis, a negative catalyst being any substance which tends to close the fields of force. (See also Baly and Marsden, *J.C.S.*, 1908, 93, 2108.)

Arrhenius was the first to point out that, on the basis of the kinetic theory, the influence of temperature would not account for an increase in the rate of chemical reaction of more than 2 per cent. per 10° C. rise of temperature. To explain the much greater effect of tem-

perature in such reactions as the inversion of cane-sugar, Arrhenius (*Z. Phys. Chem.*, 1889, 4, 226) suggested a hypothesis which, applied in another direction, had developed into his ionisation theory. He postulated the existence of "Active" and "Inactive" molecules, the former being in a condition for entering into reaction, and differing from the latter in possessing a quantity of internal energy greater than the average. These two forms were supposed in any substance to maintain an equilibrium



by a continuous interchange of internal energy. If the number of active molecules is small relative to the inactive, then a slight displacement of the equilibrium in favour of the former will much increase the velocity of any reaction in which the active molecules take part. The effect of a rise of temperature consists then in shifting the equilibrium in such a way that more active molecules are formed, in accordance with the equation

$$\frac{d \log_e K}{dT} = \frac{A}{RT^2},$$

where the constant A is taken to be one half of the energy change involved in the transformation of 1 gram-molecule of inactive to active form.

Dhar has pointed out that if active and inactive molecules exist in equilibrium, and heat, light, and catalysts augment reaction velocities by simply shifting this equilibrium, then the temperature coefficient of a reaction should be less the more positive catalyst is present (*J.C.S.*, 1911, 111, 746). Thus, if a large quantity of catalyst is present, a correspondingly large proportion of inactive molecules will be transformed to active. A rise of temperature will therefore have less additional accelerating effect because fewer inactive molecules remain to be transformed. In the same way, it follows that the presence of a negative catalyst should increase the temperature coefficient, while in the case of reactions augmented by light (photocatalytic), the temperature coefficient should diminish the greater the intensity of illumination. Several experimental results are given by Dhar to show that the temperature coefficient does vary in this way. For example, in the following photocatalytic reactions: Oxidation of Quinine sulphate by Chromic acid, reactions between Potassium oxalate and Mercuric chloride or Iodine; the temperature coefficient was shown to be greater in the dark than in light. (See also Cox, *J.C.S.*, 1921, 119, 142, and Baly and Barker, *J.C.S.*, 1921, 119, 653.)

Radiation Theory. Closely related to the ideas we have just considered is the Radiation Theory of catalysis, developed independently by W. C. McC. Lewis ("Studies in Catalysis," *J.C.S.*, 1914, 105, 2330; 1915, 107, 233; 1916, 109, 55, 67, 796; 1917, 111, 389, 457, 1086; 1918, 113, 471; 1919, 115, 182, 710, 1360; 1920, 117, 623, 1120) and Perrin (*Ann. Phys.*, 1919, (9), 11, 5).

As pointed out by Arrhenius, the influence of temperature on the basis of the kinetic theory would not account for an increase in the rate of chemical reaction of more than 2 per cent. per 10° C. rise of temperature. The observed effect is far greater, and amounts generally, in reactions proceeding near the ordinary temperature, to an acceleration of about 2½ times per 10° C. The effect of temperature must therefore be due to some influence on the internal conditions, or structure, of the reacting molecules. The same is true of catalytic influences, which bring about at constant temperature an increase of chemical reaction analogous with the effect of a rise of temperature.

He first considered the possibility of catalysts augmenting a reaction by displacing an equilibrium between active and inactive molecules in the way proposed by Arrhenius. The theory in this form was abandoned when it was found that the temperature coefficient in the hydrolysis of Methyl acetate was not lowered by increasing the concentration of catalyst (*J.C.S.*, 1914, 105, 2330. See, however, Dhar, *J.C.S.*, 1917, 111, 746, and comments by Cox, *J.C.S.*, 1921, 119, 142). Instead, Lewis developed the theory that molecules become active by absorbing quanta of energy from radiation—generally in the infra-red region—these radiations originating in the heat content of the system, or in some manner of vibration of parts of a catalyst molecule. Addition of a catalyst, or a rise of temperature, therefore, leads to greater radiation in the infra-red region, and molecules absorbing this radiation receive thereby an increment of internal energy which increases their reactivity.

Marcelin (*C.R.*, 1914, 158, 161) and Rice (*B.A. Reports*, 1915, 397) have deduced the critical increment of internal energy, E , which a molecule must obtain above its average energy before it can enter into reaction; thus,

$$\frac{d \log_e K}{dT} = \frac{E}{RT^2},$$

which is of the same form as the equation obtained by Arrhenius. It is clear that the value of E , the critical increment of internal energy, cannot be altered by mere addition of a catalyst, and this is confirmed by Lewis' experiments, which show that the temperature coefficient of a reaction is independent of the quantity of catalyst present. In the case of the hydrolysis of Methyl acetate,

the temperature coefficient is 2.5 per 10° C. increment at the ordinary temperature. Therefore, since

$$\frac{d \log_e K}{dT} = \frac{E}{RT^2}$$

$$\log \frac{K_{35^\circ \text{C.}}}{K_{25^\circ \text{C.}}} = \frac{E}{R} \left(\frac{1}{298} - \frac{1}{308} \right),$$

from which, $E = 16,800$ cal. per gram-molecule.

Now, since there are 6.85×10^{23} molecules per gram-molecule, the average energy added to a single molecule, i.e., the critical increment per molecule, expressed as the mechanical equivalent, is

$$\frac{16,800 \times 4.2 \times 10^7}{6.85 \times 10^{23}} = 1.03 \times 10^{-12} \text{ ergs.}$$

According to Einstein, a reaction which is brought about by radiant energy ("photochemically") takes place by the absorption of quanta (*Ann. Physik*, 1912, IV, 37, 832), and Lewis' theory suggests that a rise of temperature, or addition of a catalyst, supplies extra radiation, one or more quanta of which, being absorbed by reacting molecules, converts them into a reactive state.

Lewis then shows that the 1.03×10^{-12} ergs required per molecule for the above reaction can be supplied by absorbable radiation. Thus: if 1 quantum ($= h\nu$, where h is Planck's constant, $= 6.55 \times 10^{-27}$ erg sec., and ν is the vibrational frequency of this energy) is necessary to make one molecule react photochemically, Lewis calculated that

$$h\nu = 0.262 \times 10^{-12} \text{ ergs.}$$

The critical increment E per molecule is, therefore, of the order of four quanta.

Calculating the frequency ν necessary that one quantum may have the same value as E , that is, equating $h\nu$ to 1.03×10^{-12} erg, Lewis found that $\nu = 1.57 \times 10^{14}$. This radiation frequency corresponds with a wave-length of 1.9×10^{-4} cm. $= 1.9 \mu$, which actually lies within the region of infra-red absorption of Methyl acetate. It is therefore considered that radiation will account for the energy necessary to activate molecules of Methyl acetate, and that the radiation available is absorbable. Also, since the empirical equation of Arrhenius is found to hold, and the Marcelin-Rice equation is of the same form, it follows that so far as the temperature coefficient of reaction velocity is concerned the increase of internal energy necessary can be accounted for by radiation. Now if catalysis is likewise due to radiation, since this can only be produced by a vibrating charged particle, it follows that the catalyst must be

concerned in some vibration possessing a suitable frequency. In the hydrolysis of Methyl acetate with Hydrochloric acid Lewis supposed that this is due to Hydrogen ions vibrating between solvent molecules, and adduces quantitative reasoning in support of this view.

From what has been said, it will be clear that an "active" molecule is defined by Lewis as one possessing a sufficient increment of energy over the average to enable it to enter into reaction, and this increment is obtained by absorbing radiation existing in the system. In accordance with the law of mass action, the rate of a chemical reaction will then be dependent on the concentration of active molecules present in the system, and the concentration of active molecules will be proportional to the product of two factors: the concentration of the molecules as a whole, and the intensity of the radiation ("Radiation density") which renders them active. If the normal radiation density in the system is sufficient, molecules are activated and reaction proceeds, while unless the radiation reaches a certain amount no reaction can occur, whatever the concentration of the reactants. As soon as the absorbable radiation is raised to this amount, either by application of a catalyst capable of emitting radiation of the necessary frequency or by heat, reaction ensues.

Lewis has endeavoured, with considerable success, to place his theory on an exact mathematical basis. He has deduced Le Chatelier's law and the well-known reaction velocity equation, and shown also that the presence of a positive catalyst will diminish the temperature coefficient of the reaction velocity constant, while a negative catalyst will increase it. Lewis points out that these conclusions are justified by the experiments of a number of workers, viz., Von Halban (*Z. Phys. Chem.*, 1909, 67, 139; Bredig and Lichty, *Z. Elektrochem.*, 1906, 12, 459; *J. Phys. Chem.*, 1907, 11, 225; de Bruyn and Sluiter, *Proc. K. Akad. Wetensch. Amsterdam*, 1904, 6, 773, and by Francis, Geake, and Roche, who showed recently that Nitrosotriacetoneamine decomposes faster in water than in alcohol solution, and, corresponding with this, the temperature coefficient between 30° and 40° C. is smaller in the former case than in the latter, viz., $\frac{K_{40^\circ \text{C.}}}{K_{30^\circ \text{C.}}} = 2.35$ for water solution and 3.0 for Alcohol solution.

Negative catalysis is explained on the basis of the radiation theory by assuming that the negative catalyst absorbs radiation which would otherwise be available for activation of the reacting molecules. Thus, water is a negative catalyst for the action of strong Sulphuric acid on Oxalic acid, this being due to absorption by the water of the radiation, which in normal cases maintains the supply of active molecules for the reaction.

The radiation theory of catalysis we have so far developed applies more particularly to homogeneous systems. For heterogeneous catalyses Lewis accepts the adsorption theory of Langmuir, and shows that the radiation theory assists a further understanding of the mechanism (*J.C.S.*, 1919, 115, 182).

Langmuir has shown that dry Hydrogen, at very low pressures, in presence of hot metallic wires, dissociates into atoms. In this form, Hydrogen is very reactive, and is strongly adsorbed by glass and other surfaces, due, we may suppose, to the strong unsaturated affinity of the free Hydrogen atom. Oxygen likewise is powerfully adsorbed by hot metallic filaments, especially Tungsten, the adsorbed layer being exceedingly stable, and distinct from the oxide, WO_3 , formed at the same time, and which volatilises easily in comparison. Langmuir supposes that the Hydrogen and Oxygen are adsorbed in the atomic forms, and has calculated in the case of the Hydrogen that the layer is one atom deep. This dissociation into atoms, effected during adsorption by the valencies or lines of force which bind the condensed atoms to the surface atoms of the solid, is the important factor in a heterogeneous catalytic change which modifies the energy relations involved.

The velocity constants of heterogeneous reactions generally show smaller temperature coefficients than the corresponding velocity constants in homogeneous reactions. In the heterogeneous process, therefore, the critical increment is generally less than would be the case for the same process carried out homogeneously. Now the magnitude of the critical increment determines the reactivity of a substance, and also the temperature coefficient of a reaction in which it participates. The greater the value of E , the less reactive a substance will be, since more energy is required to bring it into a reactive state, and the greater will be the temperature coefficient of its reaction. The small temperature coefficient usual in heterogeneous catalytic processes is therefore directly connected with the high reactivity, and efficiency, which characterises them.

Suppose that for a given reaction the sum of the critical increments of the reactants is E_1 when the reaction is occurring in a homogeneous system and E_2 when the same reaction is taking place in presence of a heterogeneous catalyst. Then E_1 is greater than E_2 . The ratio

$$\frac{\text{Velocity constant in presence of a catalyst}}{\text{Velocity constant in absence of a catalyst}} = \frac{e^{-\frac{E_2}{RT}}}{e^{-\frac{E_1}{RT}}} = e^{\frac{E_1 - E_2}{RT}}$$

is therefore, in general, a large positive quantity. We may term it the catalytic factor. Suppose now that the reaction in question involves the dissociation of a gaseous molecule. The critical increment for this, in the homogeneous phase, would be large, and the

energy required can only be obtained by absorption of radiation. The greater the amount of energy required the higher therefore must be the temperature, in order that a sufficient number of high-frequency quanta may be available. On the other hand, if the system is heterogeneous, and a catalyst is present which is able to adsorb the gas in the atomic form, then the energy required is that of desorption of the atomic resultants, minus the energy of adsorption of the molecular reactants—a much smaller quantity. The action of a heterogeneous catalyst, therefore, is to substitute the relatively small energy terms involved in adsorption, in place of the much higher critical energies of activation or dissociation; in other words, to bring at least one of the reactants into an active form, which otherwise would only be accomplished (in the homogeneous phase) by a very high temperature.

Experimental evidence supporting the radiation theory has been adduced by Cox (*J.C.S.*, 1921, 119, 142) and by Rideal (*Trans. Am. Electrochem. Soc.*, 1919, 36, 195; *J.C.S.*, 1920, 117, 1288), who found that the catalytic hydrolysis of Methyl acetate by Hydrochloric acid is further accelerated by the action of infra-red illumination. Taylor's criticism of Rideal's work, however, is destructive (*J. Ind. Eng. Chem.*, 1921, 13, 75). Bancroft (*J. Ind. Eng. Chem.*, 1922, 14, 326) and Langmuir (*J. Am. C.S.*, 1920, 42, 2190) criticise the theory adversely and point to the almost complete lack of experimental support. Bancroft points out that the theory does not account for the same substance decomposing in several ways in contact with different catalysts, and, remarking that gum arabic is very opaque to the infra-red (Tyndall, "Fragments of Science: Radiant Heat and its Relations"), inquires whether this substance catalyses the hydrolysis of Methyl acetate. The latter implied criticism entirely lacks justice, since it is no part of Lewis' theory that all substances which absorb infra-red radiation should act as catalysts! On the contrary, it is the function of the catalyst to emit, and of a reactant to absorb.

Langmuir has calculated that the activation frequencies necessary for dissociation of Phosphine, Nitrous and Nitric oxides, Phosgene, and Phosphorus and Arsenic vapours all lie within the visible spectrum, which, since the substances in question are colourless, they are unable to absorb. He also states that, in the dissociation of Phosphine, the experimental data show that the energy required for activation is 4×10^{10} times as great as the amount that can be supplied by radiation, under certain stated conditions. Furthermore, sunlight contains radiation of a wide range of frequency, yet comparatively few reactions are accelerated by exposure to light.

To sum up. It is clear that among the numerous hypotheses that have been advanced to explain catalysis two only, the Inter-

mediate Compound theory and the Adsorption theory, have stood the test of time and possess that definiteness of conception and applicability that makes a theory useful. In the modern view, one fundamental idea these two theories possess in common: that the catalyst first associates itself chemically with one of the reacting substances, forming an intermediate complex—either a true chemical compound or a surface combination—which is more reactive than the initial substance. It must be emphasised, however, that the recognition of the intermediate stage by no means explains catalysis; it merely informs us of one step in the mechanism without making any clearer how the indirect progress of a reaction can be faster than the direct. The further explanation can only be arrived at by an understanding of the energy processes involved, and towards this the contribution of Lewis makes a noteworthy advance. The suggestion that the specific energy conferred by a catalyst is in the nature of radiant energy of definite frequency is ingenious, and full of attractive possibilities to both physicists and chemists. Its complete development must depend upon a fuller knowledge of intra-atomic and intramolecular forces, especially those which maintain vibration.

CHAPTER V

OXIDATION AND COMBUSTION

Introductory. Complete Combustion: (a) Surface Combustion. The "Bonecourt" boiler. The Incandescent Gas Mantle; (b) Selective Combustion; (c) Combustion of Carbon Monoxide, and Construction of a Carbon Monoxide Respirator. Partial Combustion: (a) Earlier Investigations; (b) Researches of Gibbs, Weiss, and Downs, and of Wohl. Partial Combustion of: (a) Naphthalene; (b) Tetrahydronaphthalene; (c) Toluene; (d) α -Nitronaphthalene; (e) Anthracene; (f) Other Substances.

Oxidation

OXIDATION reactions are invariably accompanied by generation of energy. Oxygen and oxidising agents in the presence of a body capable of oxidation are therefore highly reactive substances, and interactions involving them very prone to occur. Frequently, however, as in the case of a mixture of Hydrogen and Oxygen, the interaction is impeded by "chemical friction," which can only be satisfactorily overcome by the addition of a catalyst. Oxidation reactions which are brought about, or modified, by the presence of a catalyst, may be conveniently divided into two classes:—

1. Oxidation by air or gaseous Oxygen.
2. Oxidation effected by Oxidising agents.

Oxidation by Air or Oxygen. By far the greater number of reactions of this type may, in the broadest sense, be described as combustions, and be subdivided as follows:—

(a) Common combustion, in which Chemical reaction between a combustible substance and Oxygen is maintained by the heat generated. Contact with catalytic surfaces may, however, exercise a very considerable influence.

(b) Induced combustion. The heat of combustion alone is insufficient to maintain the reaction, except in the presence of a contact catalyst.

This division is purely arbitrary, since the presence of a catalyst facilitates combustion in both cases, but whereas in the first it merely augments the speed of a reaction already rapidly happening, in the second the augmentation is much more apparent, in that a reaction,

hardly appreciable in the absence of a catalyst, becomes self-sustaining in its presence. Many important technical reactions are cases of catalytically induced combustion; such as the contact Sulphuric acid process, the Deacon Chlorine process, the oxidation of Ammonia to Nitric acid, the manufacture of Formaldehyde from Methyl alcohol and the slow combustion "autoxidation" of metals. Under carefully controlled conditions, and in contact with certain highly specific catalytic surfaces, this combustion may be modified, and a regulated, or partial, combustion obtained. The following two chapters are devoted to this and other aspects of combustion which have not hitherto received the attention their growing importance warrants.

Other reactions involving the participation of gaseous oxygen, and which include the employment of a catalyst, are the Hargreaves, Weldon, and Weldon-Péchiney Chlorine processes, and several reactions in liquid media, such as the oxidation of aldehydes to carboxylic acids, and the "drying" of oils.

Oxidation effected by Oxidising Agents. The action of most—or perhaps all—oxidising agents can be influenced catalytically, thus: all organic compounds are first charred and finally oxidised to Carbon dioxide and water on boiling with strong Sulphuric acid. This oxidation is much facilitated by the presence of certain salts, especially Copper and Mercury sulphates. In this oxidation, Naphthalene gives a valuable intermediate product—Phthalic anhydride.

The chamber process for Sulphuric acid manufacture applies Oxides of Nitrogen, or Nitric acid, as Oxygen carriers, and provides for their continuous regeneration. The oxidising action of Nitric acid on metals and organic bodies is sometimes much increased by the addition of catalysts, such as Vanadium salts, or by the presence of Nitrous acid.

The presence of a basic oxide, or chromate, in small amount often increases the oxidising power of Chromic acid. For example, pure Chromic acid reacts imperceptibly with Carbon monoxide in the cold, but if a small quantity of Mercuric oxide is added, then the reaction is fast.

The oxidising action of Hydrogen peroxide is much modified by the presence of Ferrous salts ("Fenton's reaction"). Aniline-black is manufactured from Aniline by oxidation in presence of a catalyst, and the purification of coal gas from Sulphur compounds, especially Carbon disulphide and Sulphuretted hydrogen, depends upon selective catalytic oxidation.

Most of these reactions have been exhaustively dealt with elsewhere, and will be omitted here. This chapter will be concerned with the catalytic influences in combustion, while the next will deal specifically with the oxidation of Ammonia to Nitric acid on an industrial scale.

Combustion

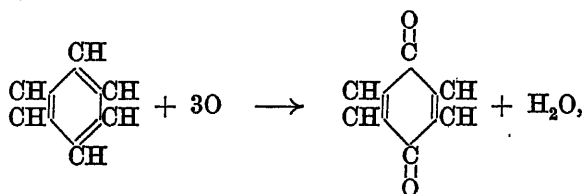
"Combustion" implies a chemical action between a substance and air, accompanied by evolution of light and heat, and usually the formation of a flame. These phenomena of burning, however, are not confined to reactions in which air or Oxygen participate, but are general when an exothermic reaction takes place between gaseous or solid substances. In the present chapter, only those reactions will be considered which are implied by the more restricted definition in which the chemical action is one of oxidation by air or by gaseous Oxygen.

An oxidation reaction is invariably exothermic, and the most exothermic reactions known are of this class. On this account, and also because air and "combustible" substances are so easily available, reactions of this type are the ones mostly applied for industrial and domestic heating. For maximum heating efficiency, that is, maximum generation of heat per unit weight of combustible substance, complete combustion must be attained, and this can be aided by catalytic means. In other cases a restricted or regulated combustion may be desired. This can be brought about by limiting the supply of air or Oxygen, in which case "incomplete combustion" results, or by the use of a specific catalytic surface which, at a carefully regulated temperature, induces the oxidation of the more easily oxidisable atomic groupings, leaving the remainder of the molecular structure untouched. This is described as "partial combustion."

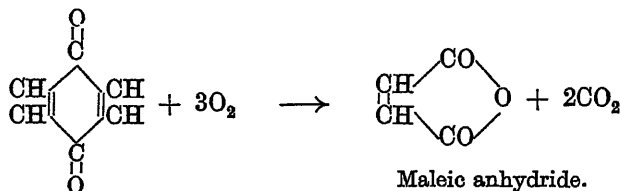
Complete Combustion consists in the resolution of a molecule into completely oxygenated fragments by reaction with air or Oxygen.

If the supply of air is insufficient for complete combustion, either less oxygenated products will result, or else a part of the substance undergoing combustion will remain unburnt. Either of these alternatives is described as *Incomplete Combustion*. Lampblack is manufactured by adjusting the supply of Oxygen so that as much as possible of the hydrogenous constituents of an organic molecule are oxidised, leaving free Carbon in a finely-divided form.

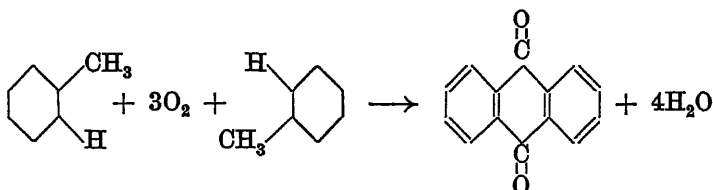
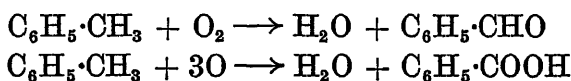
Partial Combustion is distinct from either of these, and consists in the oxidation by air or Oxygen of a part only of a chemical molecule. Thus, Benzene may be oxidised to Maleic anhydride and Maleic acid. It is probable that the Benzene molecule is first oxygenated to Benzoquinone,



(Weiss and Downs, under certain conditions also isolated small quantities of Phenol), and that two Carbon atoms are then burnt away as follows :—



Aromatic hydrocarbons containing an aliphatic side-chain can generally be made to yield mixtures of the corresponding aromatic aldehyde and acid by partial combustion. For example, using Toluene, the Methyl group is burnt away, and Benzaldehyde, Benzoic acid, and small quantities of Anthraquinone are formed :—



Many other cheap starting materials similarly yield valuable products by partial combustion. To accomplish this result, it is sometimes necessary to restrict the supply of air, but most commonly a large excess is preferable.

The effect of partial combustion, as the examples show, is to oxidise away one portion of the molecule, that is, the least stable under the particular working conditions, while the remainder of the molecule is resolved into a compound stable under the same conditions. Such a sharply-defined result, discriminating between the different stability of parts of the same molecule, requires a highly specific catalyst, and one, moreover, which, while it induces an attack on the starting material, has a much slower or inappreciable action on the product.

Complete Combustion

Any surface facilitates the combustion of a gas or vapour with air. This is a true catalytic action. The chemical and physical nature of these surfaces, however, very greatly influences their activity in this respect. Generally, a finely-divided or porous solid will be more active than a polished or a massive one, although bodies

in the latter form exert some influence—sometimes a very powerful one, as in the case of a clean Platinum wire, which in contact with air causes Methyl alcohol to inflame. Even the stablest organic substances, when mixed with air and passed over a suitable catalytic surface, will commence to oxidise at quite moderate temperatures, and the actions once started, the heat of reaction may quickly raise the catalyst to incandescence and the gases to their ignition point. Particularly active for inducing combustion of an organic vapour and air are the metals of the Platinum group and oxides of the following metals: Iron, Cobalt, Nickel, Chromium, Copper, Manganese, Silver, and Cerium.

This property of Platinum has been known for a very long time, and many instances of oxidation, aided catalytically by Platinum-black, Platinum sponge, and even by Platinum wire, have been described. The corresponding forms of Palladium behave similarly. The metallic oxides mentioned are most active when prepared by precipitation. An aqueous solution of an appropriate salt is added to excess of dilute caustic Soda solution, and the precipitated hydroxide thoroughly washed and dried. When an organic vapour mixed with air is led over either of these metal or oxide catalysts, vigorous combustion commences at comparatively low temperatures, leading to incandescence of the catalyst, and if the composition of the mixture lies within the limits for propagation of combustion, explosion follows. Matignon and Trannoy (*C.R.*, 1906, 142, 1210) impregnated asbestos fibre with these oxides by soaking it in a solution of the nitrate of the metal, drying, and igniting. They found that the impregnated asbestos so made, when heated and plunged into a mixture of ether vapour and air, remained incandescent, and Aldehyde, together with products of complete combustion (Carbon dioxide and water), were formed. Other vapours also were more or less easily attacked.

Sabatier found that Methane, one of the most stable of organic compounds, when mixed with air and passed over heated Copper oxide, Nickel oxide, or Cobaltic oxide, was completely oxidised to Carbon dioxide and water, the metallic oxide remaining incandescent after the source of heat was removed.

Certain mixtures of oxides are enormously more active than either of their individual constituents for inducing combustion of an organic substance. Such mixtures often consist of a basic and an acidic oxide mixed by precipitating the two together. Thus several mixtures described in connection with the oxidation of Carbon monoxide cause Toluene vapour and air to inflame at temperatures about 150° C. A mixture of Copper oxide and Manganese peroxide is strongly active in this respect. The activity is much increased by adding as a third constituent Ceria, Cobaltic oxide, or reduced Palladium, while "Hopcalite" (see later) is very powerfully active

indeed. This last-named substance will burst into a bright glow if a jet of coal gas is directed upon it.

The power of these mixtures of aiding combustion catalytically is quite general, though the ease with which this combustion is effected is different for different organic bodies. It depends mainly upon the stability of the organic substances in question and the "specificity" of the catalyst for the particular reaction.

Surface Combustion

The principle of surface combustion depends upon the property which all surfaces possess of promoting chemical action between gases or vapours.

In Chapter I we have described the experiments of Davy and Erman in which they showed that a warmed Platinum surface introduced into a mixture of a combustible vapour and air became incandescent by the flameless combustion of the gases at its surface. The conditions necessary to maintain a body at a high temperature by surface combustion were first investigated by Fletcher (*J. Gas Lighting*, 1887, 1, 168), who showed that a mixture of coal gas and air, of carefully regulated composition, could be brought continuously into contact with a bundle of hot Iron wire in such a way as to keep the wire at a high temperature without any sign of flame. Surface combustion can be demonstrated as follows: Jets of a combustible gas and air are made to impinge upon the surface of a porous refractory mass, such as firebrick. The gas is then ignited, and the air current adjusted to deliver slight excess over that required for complete combustion. When the refractory mass attains a high temperature, the proportions of gas and air and their mode of admittance can be so arranged that the flame becomes first non-luminous, diminishes in size, then retreats to the surface of the heated mass, and finally disappears altogether. Combustion now is confined to the surface of the mass, which glows brightly while there is no flame.

The catalytic effect of various surfaces at high temperatures in promoting combustion has been systematically studied by Bone (1902 onwards), and the technical developments of surface combustion, largely due to Bone and his co-workers, especially McCourt, are the direct outcome of these experiments. Work on the same lines by Schnabel was simultaneously in progress in Germany (*Ber.*, 1913, 46, 5). The whole subject from its inception to its technical application was expounded by Bone in a series of lectures before the Society of Arts, London, in March 1914 (*J. Roy. Soc. Arts*, 1914, 62, 787, 801, and 818).

The first type of surface combustion heater consisted of a porous refractory diaphragm, mounted gas-tight in an iron frame, which formed a side of an iron box. A mixture of air and a combustible gas, in the proportions requisite for complete combustion, was

delivered into the box by a blower, and forced through the diaphragm. On igniting the gas mixture at the outside surface, the firebrick soon commenced to glow brightly and radiate heat intensely. The gas was completely burnt in passing the diaphragm, and there was no noise or sign of flame.

With apparatus of this description it was possible to burn completely all the combustible constituents of any gas mixture, *e.g.*, water gas, producer gas, coal gas, petrol or benzol vapour, or even blast-furnace gases, with a very high efficiency, since combustion was complete and localised, so that almost the entire calorific value of the fuel was obtained as useful (mostly radiant) heat. An oven heated in this way attained cooking temperature (150–200° F.) in about one-third the time required when an equal flow of gas was burnt in the usual way. The apparatus was convenient, since it could be placed in any position, clean, and the effluent gases, consisting only of Nitrogen, Carbon dioxide, and water vapour, harmless. The disadvantages that have prevented diaphragm combustion obtaining a much wider application are the difficulty of preventing backfiring, the necessity of supplying the gases at a pressure sufficient to penetrate the diaphragm, and the tendency for tar-spray and dust in technical gases to clog the diaphragm. Cox has largely overcome these difficulties by careful selection of the diaphragm, and using tar and dust-free gases (Tulloch, *J.S.C.I.*, 1926, 45, 280t). Thus, a suitable diaphragm, mounted by gas-tight joints into the side of an Iron mixing chamber, was fed with coal gas and air at pressures only slightly above the atmospheric. The pressure of the coal gas (at about 4 inches water gauge) was slightly above that of the air (about 3 inches), and the mixing took place in the supply pipe a few inches from the mixing chamber, by using an injector tube-piece for the gas. It was found that by using this apparatus the gas pressure could be allowed to fall very low without danger of back-firing.

Using technical gases, Bone and McCourt's chief source of difficulty was due to the choking of the diaphragm with dust and tar. In place of the diaphragm they therefore substituted a bed of refractory packing, which they placed round the muffle, retort, or crucible which they wished to heat, or within the tubes of boilers. The method proved very efficient, but the difficulty of back-firing was not completely overcome. It is understood that this also has been met by Cox, who, instead of a uniform packing, uses granules of refractory materials of smaller mesh towards the entrance end (Tulloch, *loc. cit.*). Combustion then takes place in a localised zone. The smaller granules coming before this zone prevent back-firing and preheat the gases, while the larger lumps coming later aid in transferring the heat from the products of combustion to the crucible, or boiler, or whatever vessel it is desired to heat.

When flameless, incandescent, surface combustion is brought about at the bounding surface between a solid and a combustible gaseous mixture, by injecting the latter upon, or forcing it through, the former, Bone found that :—

1. All surfaces accelerate gaseous combustion, but in varying degrees, according to their chemical nature and physical condition.

2. The power of a hot surface for accelerating gaseous combustion increases as the temperature rises. At the same time, surfaces which have very different activities at low temperatures tend to become equal as the temperature rises, so that at bright incandescence all surfaces are more or less equally effective.

3. The acceleration of surface combustion depends on adsorption or occlusion of the combustible gas, and sometimes of Oxygen. The gases are thereby brought into intimate contact under conditions which lead to their ionisation and "activation."

4. The surface becomes electrically charged during the process of surface combustion, due presumably to the discharge of electrons from the incandescent mass.

5. The combustion does not take place uniformly throughout the mass, but in layers. Within a diaphragm, the zone of combustion is surprisingly thin—not more than $\frac{1}{8}$ to $\frac{1}{4}$ inch.

The technical results of Bone's work are described in a series of papers in the *Journal of Gas Lighting* commencing in 1909, and in his patent specifications. Kunzbrunner ("Fuerungstechnik," I, 62-7, 118-20, and 259-62) reviews the various theories advanced in connection with flameless or surface combustion. His own view is, that a self-regulation of the combustion zone occurs within the porous mass, which assists by catalytic action the combustion within a restricted space of large quantities of gas and air in theoretical proportions.

The Surface Combustion ("Bonecourt") *Boiler* (Bone, Wilson, and McCourt, E.P. 29430 of 1909). Combustion is made to take place at the surfaces of lumps of refractory material, which are packed into the tubes of the boiler. The best refractories are calcined Magnesia or Carborundum, but more recently, to reduce the inefficiency that may result from the use of industrial gases containing dust or tar, other packings of various materials and form have been proposed (Bone and Kirke, *J.S.C.I.*, 1919, 38, 228r).

By burning 100 cubic feet of coal gas and 550 cubic feet of air in a 3-foot iron tube, 3 inches internal diameter, packed with a granule refractory, nearly 100 lb. of water per hour were evaporated, or 20-22 lb. per square foot of heating surface. This represented a heat transmission to the water of 88 per cent. of that generated by the combustion, comparing with 50 to 70 per cent. when blast furnace gases or coke oven gases are used by the ordinary method of firing.

The first experimental surface combustion boiler, installed at the Skinningrove Iron Works in 1911, consisted of a boiler drum 10 feet in diameter and 4 feet long, fitted with 110 tubes of the size just described. After 5 months' working this boiler gave an efficiency ratio

$$\frac{\text{Heat utilised}}{\text{Heat supplied}} = 0.927,$$

while the burner gases, leaving at 170–200° C., carried away only 3 per cent. of the total heat generated (much of this was subsequently recovered by preheating the boiler feed water). A number of surface combustion boilers have since been installed, and an efficiency ratio of over 90 per cent. regularly obtained. The details have been published by Bone and Kirke (*loc. cit.*). The difficulty of preventing back-firing of the gases has hitherto stood in the way of their more extensive use. With this overcome (see Tulloch, *loc. cit.*), the economic possibilities of the surface combustion boiler would seem to be very great indeed.

Diaphragm heating has been used on a large scale for evaporation, with considerable saving of gaseous fuel (Bone, *J. Gas Lighting*, 1914, 125, 572). Furnaces for melting metals have been constructed consisting essentially of a crucible surrounded by a granular porous refractory, heated by passage of a combustible gaseous mixture. In gas fires, used for domestic heating, combustion of gas takes place at the surface of a porous refractory which radiates a high proportion of its heat to the surrounding air.

The Incandescent Gas Burner. This is arranged so that a mixture of gas and air burns without flame at the surface of the mantle. The action of the mantle is catalytic, and comparable with the other instances of surface combustion described.

The production of light by raising a refractory material to incandescence is a practical problem that has engaged the attention of many experimenters. The earliest form was the "limelight," based on the experiments of Drummond, who raised surfaces of Lime, Magnesia, or Alumina to incandescence by means of an Oxy-Hydrogen flame. Berzelius first pointed out that Thoria and Zirconia were much more powerful light emitters in the Oxy-Hydrogen flame than either of the above-mentioned oxides. The use of a bunsen flame as a possible source of incandescent light was investigated by many workers, but it was not until 1880 that Williams, in America, and von Welsbach, in Austria, simultaneously discovered the secrets which led ultimately to technical success.

During his researches on the crystallisation of the "rare earths," commencing in 1880, Welsbach noticed that when cotton threads were soaked in a suitable solution of a rare earth salt, then dried, and the cotton burnt, a coherent ash consisting of the "earth" remained.

The difficulties were, however, still numerous. Irregularities in the cotton fibre rendered the resulting ash unreliable and weak, and tending to crumble. The composition of the mantle very much affected the colour and intensity of the flame. Many substances which greatly improved the light emissivity of the mantle were too volatile, and, due to their accidental inclusion, a continuous falling off in light-emitting power occurred during use.

In 1886, Welsbach patented the use of Thoria (D.R.-P. 41945), believing at this time that Thoria possessed a very high power of light emissivity. Later, however, he found that pure Thoria was a comparatively feeble illuminant, the brilliant luminosity in the earlier results being due to the presence of small quantities of Ceria as impurity. He found that the mantle developed its maximum emissivity of light when the composition was 99 per cent. Thoria and 1 per cent. Ceria, and mantles are now made of Thoria and Ceria in these proportions. A higher percentage of Ceria again reduced the light-giving properties of the mantle, so that with 10 per cent. of Ceria the luminosity was again small.

The explanation of these facts is catalytic. Brightness is greater the more completely the combustion is localised within the material of the mantle, since in this way the mantle is raised to the maximum temperature possible, and therefore develops its strongest incandescence. Why the mixture of 99 per cent. Thoria with 1 per cent. Ceria possesses the specific catalytic properties necessary is (like all similar questions in catalysis) quite unknown, although numerous hypotheses have been put forward.

The gradual diminution in light emissivity which occurs with continued use was ascribed by White and Müller (*J. Gas Lighting*, 1903, 83, 504) to the volatilisation of the Ceria, while Bruno (*Z. f. Beleucht.*, 1899, 5, 244) attributed it to the transformation of the Ceria into an allotropic form, and stated that the inert form could be reconverted into the active by slow cooling.

Many other substances have been proposed for addition to the mantle composition, some for purpose of increasing the durability, and others for imparting additional light-emitting properties. For strengthening, small quantities of Glucina, Alumina, and Magnesia have been used, and for increasing the light emissivity, oxides of metals which are capable of many stages of oxidation, and which can therefore function as "Oxygen carriers," such as oxides of Manganese, Iron, Cobalt, Chromium, Vanadium, and Uranium. Lanthana and Lime have also been employed. Of these substances, several have been found unsatisfactory in practical use: for example, the oxides of Magnesium, Iron, and Cobalt are distinctly volatile, and Lime is attacked by atmospheric Carbon dioxide and moisture while the mantle is idle.

Selective Combustion

A combustible gas, present in air in a small proportion (less than 1 per cent.) is difficult to burn completely except with the help of a catalyst. A glowing Platinum wire or hot granules of Copper oxide are often used to effect complete combustion in such cases—as, for example, in processes of gas analysis, and their action is at least partly catalytic.

Commonly, catalytic combustions are susceptible of such delicate control that in a mixture of several combustible gases with air, by employing a suitable catalyst, and working at a carefully regulated temperature, one of the gases can be completely burnt, while others are unattacked. For instance, if Methane and Hydrogen are led over Copper oxide at 320°C. , only the latter is oxidised. The same effect is produced by leading a mixture of Methane, Hydrogen, and excess of air over finely-divided Copper at the same temperature.

Finely-divided Palladium, *e.g.*, palladinised asbestos, at temperatures up to about 300°C. , has no action on a mixture of Methane and air. Hydrogen, however, is quickly burnt, even at 100°C. under the same conditions, and the catalyst may burst into a brilliant glow. This difference in behaviour enables an accurate analysis of mixtures of Hydrogen and Methane to be quickly made.

Rideal and Taylor (*Analyst*, 1919, 44, 89–94; E.P. 134243 of 1918) described a method for the preferential combustion of Carbon monoxide in mixtures of this gas with Hydrogen. Their catalyst consisted of a mixture of Iron and Chromium oxides, to which small quantities of Ceria and Thoria had been added. Between 200°C. and 300°C. , with excess of air, this catalyst oxidises Carbon monoxide completely, but does not attack Hydrogen.

Catalysts which actively promote the oxidation of Carbon monoxide at 0°C. and have been used in Carbon monoxide respirators do not cause Hydrogen and Oxygen to combine below 70°C. This may be due to the anticatalytic action of the water formed, since it has been shown that specially dried “Hopcalite” at 0°C. commences to burn Hydrogen, but that the action soon stops. Lamb has shown that if sufficient Oxygen is provided a dry gas mixture can be completely purified from Carbon monoxide by use of “Hopcalite,” and has suggested that this catalyst might be employed to remove the last traces of Carbon monoxide from the gas mixture used in the synthesis of Ammonia (*J. Am. C. S.*, 1922, 44, 738; 1925, 47, 123). Selective combustion has been proposed in other cases as a convenient means of eliminating small quantities of a gas from a mixture. For example, Phosphine poisons a Platinum catalyst in the Ammonia oxidation process for the manufacture of Nitric acid. Parsons (E.P. 136342 of 1919) proposed to eliminate Phosphine from the Ammonia—

air mixture by passing it over a powerfully active oxidising catalyst at a temperature below 100° C. Silver oxide, impregnated upon absorbent Charcoal, and subsequently reduced in a current of Hydrogen, was proposed. Under these conditions, Ammonia is stable, but Phosphine oxidises to Ammonium phosphate.

Combustion of Carbon Monoxide

During the war, Carbon monoxide poisoning became serious, owing to the large quantities of this gas produced in detonation of propellant and high explosives. Symptoms of poisoning by Carbon monoxide were especially prevalent in Naval gun turrets, in enclosed machine gun emplacements ("pill boxes," "tanks," etc.), and during mining and sapping operations. The need for a respirator effective against Carbon monoxide became pressing, and investigations were carried out in this country by the present author and a number of collaborators, and simultaneously in America by chemists of the United States Chemical Warfare Service.

It was found that certain oxides, when properly made, induced reaction between Carbon monoxide and air at the ordinary temperature, and that some mixtures of oxides with promoters were sufficiently active in this respect to serve as the basis for a Carbon monoxide respirator.

Oxides of the following metals, when properly prepared, induce combustion of Carbon monoxide with air at relatively low temperatures: Copper, Iron, Nickel, Cobalt, Manganese, Silver. Finely-divided metals of the Platinum group, especially Platinum and Palladium, are also powerfully active. The reaction in each case commences below 100° C., while with Silver oxide, "Nickelic" oxide, and Palladium-black it is appreciable at the ordinary temperature. Copper oxide gives a just measurable action at 20° C., and Manganese peroxide, when made by a special method, is active at 0° C.

Certain mixtures of these oxides, and especially those in which a basic oxide is mixed with an acidic oxide, are enormously more active than either constituent taken singly. For instance, the following mixtures when properly made induce rapid reaction between Carbon monoxide and air at the ordinary temperature: Copper oxide and Manganese peroxide, Silver oxide and Manganese peroxide, Copper oxide and Ferric oxide, Higher oxides of Nickel, Cobalt, or Iron with Manganese peroxide.

The activity of these mixtures can be still further enhanced by the addition of a promoter. Effective promoters are oxides of certain of the rare-earth metals, especially Ceria, and certain finely-divided metals, among which Palladium and Silver may be mentioned.

It must here be noted that the union of Carbon monoxide and

Oxygen in contact with these oxides is not always entirely catalytic. Sometimes the oxidation is partly chemical, peroxides employed in the contact agent supplying the Oxygen, and partly catalytic. The more satisfactory the preparation of the catalyst, the more completely catalytic the reaction becomes.

The action of Chromic acid on Carbon monoxide may be conveniently described here, although the catalytic phenomena involved are of an entirely different character. When a mixture of Carbon monoxide and air is passed over moist, powdered Chromic acid at the ordinary temperature, little or no oxidation takes place. If, however, the moist Chromic acid is ground up with yellow Mercuric oxide, Copper oxide, or higher oxides of Nickel or Cobalt, then Carbon monoxide is vigorously oxidised even at 0° C. Oxygen of the air is not here involved, but only the Oxygen of the Chromic acid, activated by the presence of the basic oxide.

In the experiments tabulated below, a mixture of Carbon monoxide and air, containing approximately 2 per cent. of the former, was passed at a measured rate over granules of the catalyst, which was maintained at the ordinary temperature, and which filled a tube 20 cm. long and 1.5 cm. internal diameter.

| Catalyst. | Prepared from | Rate of passage of CO-air mixture. (C.c. per hr.). | Per cent. CO. | |
|--|--|--|---------------|----------|
| | | | Entering. | Leaving. |
| Ag ₂ O . . . | AgNO ₃ , NaOH | 800 | 2.00 | 0.29 |
| HgO . . . | HgCl ₂ , NaOH | 800 | 2.53 | 2.51 |
| CuO . . . | CuSO ₄ , NaOH | 800 | 2.00 | 1.95 |
| MnO ₂ . . . | MnCl ₂ , NaOH, Cl ₂ | 800 | 2.53 | 2.09 |
| MnO ₂ . . . | MnSO ₄ , KMnO ₄ and H ₂ SO ₄ | 4,000 | 1.97 | 0.80 |
| Nickel oxide . . | Ni(NO ₃) ₂ , NaOH and Cl ₂ | 800 | 2.25 | 0.06 |
| Cobalt oxide . . | Co(NO ₃) ₂ , NaOH and Cl ₂ | 800 | 2.53 | 0.16 |
| HgO + MnO ₂ . . | HgCl ₂ , MnCl ₂ , NaOH and Cl ₂ | 18,000 | 2.27 | 0.07 |
| HgO + Fe ₂ O ₃ . . | HgCl ₂ , FeCl ₃ , NaOH and Cl ₂ | 1,000 | 2.27 | 0.08 |
| CuO + MnO ₂ . . | CuSO ₄ , MnCl ₂ , NaOH and Cl ₂ | 800 | 2.45 | 0.39 |
| Ag ₂ O + MnO ₂ . . | MnCl ₂ , NaOH and Cl ₂ , AgNO ₃ and NaOH made separately. | 800 | 2.28 | 0.17 |
| HgO + CrO ₃ | { The basic oxide was ground with moist Chromic acid } | 800 | 2.35 | None |
| CuO + CrO ₃ | | 800 | 2.91 | 1.90 |
| Cobaltic oxide + CrO ₃ | | 800 | 2.35 | None |

Taking the $\text{CuO} + \text{MnO}_2$ mixture, and adding as a third constituent either Ceria, Cobaltic oxide, reduced metallic Palladium, or Silver oxide, the activity became much too great to compare with the previous results, by the method indicated.

Preparation of the Catalyst. Oxides and mixtures which gave the results just described were made in all cases by precipitation. The nitrate, chloride, sulphate, or other soluble salt of the metal was dissolved in water, and the cold dilute solution added slowly, with stirring, to excess of a cold dilute solution of caustic Soda or Ammonia. To make a mixture of two or more oxides, dilute solutions of the appropriate metallic salts were first mixed, and the mixture was then added to the alkali, so that the oxides were precipitated in contact. When one of the constituents of the desired mixture was Cobaltic, Nickelic, or Manganese peroxide, the precipitation was carried out while a steady stream of chlorine was passing into the caustic Soda, which was then present in correspondingly greater excess.

After precipitation, the hydroxides were thoroughly washed with tap water. The washed hydroxides were filtered, and a preliminary drying was carried out at 100°C . The cake, dried at 100°C ., was generally hard, and easily granulated. The granules were then completely freed from uncombined water by heating for several hours at $150\text{--}170^\circ \text{C}$. The presence of uncombined water greatly lowers the ordinary temperature activity of these catalysts, so that complete drying and damp-tight storage are essential. Since they are somewhat hygroscopic, holding in the hand quickly destroys their low temperature activity, which, however, can be restored by again heating to 150°C .

Prolonged heating at $150\text{--}200^\circ \text{C}$. leaves much chemically combined water, which is only slowly given up at this temperature. This, however, is no disadvantage. Its complete removal requires such powerful heating that the extreme activity of the catalysts is destroyed.

The fact that the most active catalysts are mixtures of basic oxides with oxides that are capable of functioning as acids suggests that the active agent is possibly a compound formed between them. Conditions of preparation which might be expected to favour reaction between the two oxides certainly are favourable for the formation of a very active catalyst. Moreover, Fe_2O_3 can serve as a useful constituent of a mixture if precipitation is carried out in a way conducive to formation of ferrates.

Construction of a Carbon Monoxide Respirator. The catalyst obtained by the present author and collaborators consisted of a mixture of Copper oxide, Manganese peroxide, and 1 to 5 per cent. of Ceric oxide as promoter. This was prepared by dissolving

equimolecular proportions of Copper sulphate and Manganese sulphate in water and running the mixed dilute solution of the two into excess of cold dilute caustic Soda, meanwhile stirring the latter solution, and passing in a steady stream of Chlorine. Passage of Chlorine was continued until the solution showed the colour of Permanganate. The precipitate was then thoroughly washed by decantation. Independently, a dilute solution of Cerium sulphate was added to a freshly-mixed ammoniacal Hydrogen peroxide solution. The orange precipitate so obtained was completely washed. The two washed precipitates, while still in suspension, were then well mixed, filtered, and dried at 100°C ., then granulated, and freed from uncombined water at $150\text{--}170^{\circ}\text{C}$.

About the same time, the American Chemical Warfare Service brought out the catalyst "Hopcalite," a mixture of the following composition:—

| | | | | | |
|--------------------|---|---|---|---|--------------|
| Cupric oxide | . | . | . | . | 30 per cent. |
| Manganese peroxide | . | . | . | . | 50 " |
| Cobaltic oxide | . | . | . | . | 15 " |
| Silver oxide | . | . | . | . | 5 " |

(Lamb, Bray, and Frazer, *Ind. Eng. Chem.*, 1920, 12, 213; Rogers, Piggot, Bahlke, and Jennings, *J. Am. C.S.*, 1921, 43, 1973; Merrill and Scalione, *ibid.*, 1982; Almquist and Bray, *ibid.*, 1923, 45, 2305; Whitesell and Frazer, *ibid.*, 2841; Lamb, Scalione, and Edgar, *ibid.*, 1922, 44, 738; Lamb and Vail, *ibid.*, 1925, 47, 123).

The most important constituent, the Manganese peroxide, was originally made by reduction of Ammonium permanganate with Methyl alcohol. Later, the Frémy method (*C.R.*, 1876, 82, 1231) was substituted, since it was found to give a more active oxide. In this method, powdered Potassium permanganate is treated with cooled 60—66 per cent. Sulphuric acid and allowed to stand for several days. As soon as the Permanganic acid has decomposed, the mixture is poured into excess of water and the precipitated Manganese peroxide washed free from sulphates by repeated decantation. The product is very finely divided, and when dry induces powerful catalytic action between Carbon monoxide and air. Finally it was found that a still more active Manganese peroxide was obtained when Manganese sulphate and Potassium permanganate interacted in warm, fairly concentrated Sulphuric acid solution, as follows: 150 grams of very finely-powdered Manganese sulphate were mixed rapidly with 142 grams of water, and strongly cooled, and agitated while 675 grams of 93 per cent. Sulphuric acid were run in. With the mixture at about 50°C ., 150 grams of coarsely-powdered Potassium permanganate were then added in small quantities at a time

during about half an hour, carefully keeping the temperature below 75°C . After allowing the reaction to complete—which required about 15 minutes—the Manganese peroxide was thoroughly washed with cold water by decantation and stored as a thin paste.

The Copper oxide was made by precipitation of the hydroxide or carbonate from Copper sulphate solution in the ordinary way. After washing, the precipitate was stored as a thin paste.

The Cobalt oxide was made from Cobalt sulphate solution by adding a solution containing excess of caustic Soda and Sodium hypochlorite. This precipitate was washed, and stored as before.

Correct quantities of the suspensions of the three oxides, Manganese peroxide, Copper oxide, and Cobaltic oxide, were then mixed in excess of water, and a small quantity of pure caustic Soda solution (free from chloride) was added. The correct quantity of Silver nitrate, made to a dilute solution in distilled water, was then run in, during agitation. Silver oxide in this way was deposited in intimate admixture with the other oxides. After again thoroughly washing, the precipitated oxides were filtered, pressed, dried at 100°C ., granulated, and completely dried at 200°C .

A catalyst made by either of the methods described consists of hard and durable granules, which induce rapid action between Carbon monoxides and air, with generation of heat. The heat of reaction is so considerable that when a respirator is used against a 2 per cent. mixture of Carbon monoxide in air, provision must be made for cooling before the air can be inhaled. The American investigators devised a cooler, which consisted of a sealed canister, filled with a low melting solid of high latent heat of fusion. Crystalline Sodium thiosulphate was the substance chosen, and the hot air passing was cooled approximately to the melting point of Sodium thiosulphate.

In addition to the catalyst granules and cooler, the complete respirator also contained a desiccating agent, generally granular Calcium chloride, over which the incoming gases were made to pass before contact with the catalyst. Such a respirator was compact, being not much larger or heavier than the British service respirator, and its effective "life" depended mainly upon the satisfactory working of the drying agent. When this was renewed sufficiently often, elimination of Carbon monoxide was complete for a long period.

Partial Combustion

When a combustible organic compound is mixed with excess of air, and passed over a highly active oxidising catalyst, it is usually impossible to stop the action at any stage short of complete combustion. For instance, when an organic vapour with excess of air

is passed over a finely-divided oxide of Iron, Cobalt, Nickel, Manganese, Copper, or a mixture of these, if the temperature is sufficiently high to induce reaction, then complete combustion ensues, with the formation of minute amounts only of products of partial combustion. If the supply of air is limited, the quantity of partial combustion products tends to increase, but not much, the main resultants being unchanged initial material, Carbon dioxide, and water. To obtain products of partial combustion in appreciable yield, it is necessary to select a contact agent of only moderate power, that is, one which possesses oxidising properties, but does not induce oxidation of combustible substances at equally rapid rates. For example, the oxides mentioned are so energetic that combustion of all substances is effected at a rate too rapid to control. When, however, these oxides are combined with weakly acidic ones, such as Phosphoric, Arsenic, Silicic, Boric, or Tungstic, then their powers are so much moderated that it becomes possible to isolate products of partial combustion by suitable adjustment of temperature and time of contact. The usual oxidising catalysts, however, and these possess a specific influence in this direction—just as Alumina and Thoria exert a specific dehydrating action—are the oxides of metals of the fifth and sixth groups of the Periodic table, especially Vanadium pentoxide, and Molybdic and Tungstic oxides.

For a satisfactory partial combustion the conditions must be carefully regulated, especially the temperature of the catalyst, and the space velocity of the reacting gaseous mixture. A temperature too high, or too prolonged a period of contact, increases the proportion of complete combustion, and correspondingly lowers the yield of the desired product. Since all partial combustion reactions are strongly exothermic, the temperature regulation becomes in practice the most difficult to control. Evenness of heating, and a uniform temperature gradient throughout the catalyst are vital, while the exact temperatures and other conditions must be adapted to each particular reaction. Any tendency to local overheating of the catalyst must be avoided, especially in large scale working, since local overheating causes increased reaction in that locality, leading in turn to still greater local heat development. Thus, temperature irregularities tend to be increased by the heat of reaction, and eventually lead to decomposition, or complete instead of partial combustion. As emphasising the importance of these points, the following experience may be cited. Naphthalene vapour and air, containing too high a proportion of the former, were being passed over heated Vanadium pentoxide, mounted on pumice. The arrangements for temperature control of the catalyst were inadequate, with the result that in a short time both catalyst and pumice had fused.

Earlier Investigations on Partial Combustion of Organic Substances. Considering the striking economic possibilities of reaction of this type, it is strange that so little research has been devoted to them until recently. A résumé of the work on this and allied subjects up to the year 1920 is given by Weiss and Downs (*Ind. Eng. Chem.*, 1920, 12, 228).

Coquillon (*C. R.*, 1875, 80, 1089) passed Benzene and Toluene vapours mixed with air through a tube containing an incandescent Platinum wire, and found Benzaldehyde and Benzoic acid among the products. It is probable that the Benzene used contained Toluene as impurity, since the formation of Benzaldehyde and Benzoic acid from Benzene is otherwise difficult to understand.

The first important investigations were those of Walter (*J. pr. Chem.*, 1892, 45, 107), who, using Vanadium pentoxide as catalyst, described the oxidation of Toluene to Benzaldehyde and Benzoic acid, and of Anthracene to Anthraquinone. He also stated that Alcohol is oxidised to Acetaldehyde and Acetic acid, Diphenylamine to Carbazole, Benzene to Diphenyl, and petroleum to a complex mixture. Walter's work was purely qualitative, but indicated the great potentialities of the reactions examined. They were afterwards protected by the following patents: D.R.-P. 168291 of 1904, F.P. 360785 of 1905, E.P. 21941 of 1905.

Commencing in 1907, Orlov published an important series of papers, largely theoretical, but including accounts of several investigations, particularly relating to oxidation of alcohols (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 855, 1023, 1414; 1908, 40, 652, 659, 796, 799, 1590, 1596; *Z. Phys. Chem.*, 1909, 69, 499). Orlov's results have been collected into the following two books, "Der bisherige Stand der wissenschaftlichen Erkenntniss und der technischen Verwendung sowie neue Untersuchungen über seine Herstellung und über pyrogenetische Kontaktreaktionen" (Barth, Leipzig, 1909) and "Formaldehyde" (Barth, Leipzig, 1909).

Woog (*C. R.*, 1907, 145, 124) obtained Benzaldehyde from Toluene and air, in the vapour phase, by the action of Platinum and other catalysts.

Chavy, Delage and Woog (F.P. 379715 of 1907) passed Toluene vapour and air over oxides of Copper, Iron, Nickel, or Cobalt, and obtained Benzaldehyde, mixed with a little Benzoic acid. A wider choice of catalysts was stated to be available for the formation of Benzoic acid.

F. Beyer und Co. (D.R.-P. 278647 of 1912) claimed that Erythrene was produced by the incomplete combustion of many organic substances, among which were Benzene, Toluene, and Naphthalene.

Recent Work on Partial Combustion of Organic Substances. The first systematic research was carried out by H. D. Gibbs and col-

laborators, of the United States Bureau of Chemistry. The catalytic oxidation of numerous organic compounds was investigated, and patents have appeared covering the following reactions: Naphthalene to Phthalic anhydride; Anthracene to Anthraquinone; Phenanthrene to Phenanthraquinone; and Toluene to Benzaldehyde and Benzoic acid.

More recently, Weiss and Downs, also in America, have investigated the same reactions, and also the partial combustion of Benzene; while Wohl, in Germany, has given exact details for the partial combustion of Naphthalene to Phthalic anhydride.

The results obtained by these investigators will be considered in detail in connection with the reactions concerned.

The Partial Combustion of Naphthalene

The formation of Phthalic anhydride from Naphthalene was discovered by Gibbs and Conover, who protected the reaction by the following patents: U.S.Ps. 1284887, 1284888, and 1285117 of 1918; E.Ps. 119517 and 119518 of 1917. Since 1917, numerous patents and several papers have appeared, as follows: Gibbs, E.Ps. 14150 and 14151 of 1917; Canadian Ps. 186444 and 186445 of 1918; U.S.Ps. 1288431 of 1918 and 1303168 of 1919; *Ind. Eng. Chem.*, 1919, 11, 1031; Selden Co., E.P. 170022 of 1920; Wohl, E.P. 145071 of 1920; Weiss and Downs, U.S.Ps. 1374695, 1374720-2, and 1377534 of 1921; Conover and Gibbs, *Ind. Eng. Chem.*, 1922, 14, 120; Kusama, *J. Chem. Soc. Japan*, 1923, 44, 605. Craver & Barrett Co., U.S.P. 1489741 of 1924.

Apparatus. For laboratory or research purposes, a type of apparatus similar to that described by Gibbs (*Ind. Eng. Chem.*, 1922, 14, 121) is satisfactory. Air, filtered by passing through cotton wool but not otherwise purified, is passed at a measured rate over the surface of melted Naphthalene, maintained at a steady temperature by immersion in a brine bath. By adjusting the temperature of the bath, the proportion of Naphthalene picked up by a constant air stream can be fixed as desired, since in the same apparatus this proportion depends only on the temperature of the bath and the rate of the air-stream. The Naphthalene-laden air passes thence through tubes warmed electrically by a fine coil, to prevent decomposition of Naphthalene, to the catalyst chamber. A silica tube, about 3 feet long and 1 inch in internal diameter, branched near the exhaust end, is convenient. Connections may be made by means of rubber bungs and tubing, so long as the silica tube is of suitable length, since the vaporiser and leading tubes need not be heated beyond 130° C. Gibbs used a pyrex glass tube and ground glass joints. The reaction products pass by the branch to a condenser, while pyrometer wires are inserted through the straight end. These

wires are protected and insulated by enclosing in thin glass tubes, while the junction of the wires is embedded in the catalyst. A wide, air-cooled glass tube, 2 feet long, plugged loosely with cotton wool at the exhaust end, easily condenses and retains all the solid reaction products. The reaction tube is heated by enclosing in an electrically-heated copper tube lined internally and externally with heat-insulating material (Fig. 2).

Catalyst. The first patents taken out by Gibbs specified oxides of metals of Groups V and VI of the periodic table, mentioning in particular oxides of Vanadium and Molybdenum. This vague claim was defined more precisely in later announcements. Vanadium pentoxide was shown to be far better than any other single oxide,

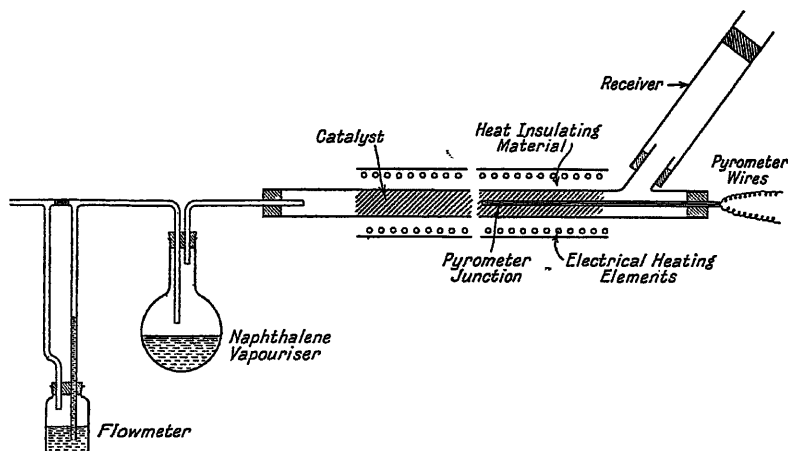


FIG. 2.

and capable of producing Phthalic anhydride in yields of 80–85 per cent. of theory.

Molybdenum oxide, MoO_3 , gave yields of 50–60 per cent. of theory, while Tungstic oxide was capable of producing yields up to 20 per cent. of theory. Numerous other oxides have been found to give small quantities of Phthalic anhydride, but the only catalysts economically possible are Vanadium pentoxide, Molybdenum oxide, or a mixture of several oxides in which one or both of these substances is present. Vanadium pentoxide may be made by either of the following methods: (a) By heating Ammonium vanadate until the Ammonia is completely driven off. (b) By precipitating Vanadic acid from a solution of a metallic vanadate in water. The solution of vanadate should be boiled, and strong Nitric acid added drop by drop to the boiling solution until slight excess is present. The red precipitate of Vanadic acid gives Vanadium pentoxide on heating. (c) By decomposing the nitrate, or either of the chlorides of Vanadium, with water or steam.

Prepared by methods (b) or (c), thorough washing of the precipitated Vanadium compound is necessary before drying and heating.

Vanadium pentoxide made by either of these methods can be mounted on a support, *e.g.*, pumice, asbestos, or a metallic support, which, on account of its high conductivity for heat, possesses certain advantages in a strongly exothermic reaction.

Gibbs has shown that finely-divided Vanadium pentoxide does not give so good a yield of Phthalic anhydride as the coarser form that has been sintered by heating to about 550° C., or fused, and powdered. This has been confirmed by other workers. Thus, when prepared from Ammonium metavanadate by heating to temperatures of about 300° C., Vanadium pentoxide is a light chocolate-coloured powder. The highest yield of Phthalic anhydride obtainable, using Vanadium pentoxide in such a form, is less than 70 per cent. of the theoretical. When heated to about 550° C., Vanadium pentoxide becomes darker in colour, apparently sinters, and becomes much less fine. At 658° C., Vanadium pentoxide melts, and on cooling resolidifies to a dark bluish-black, crystalline mass. In either of these forms, sintered by heating to 550° C., or fused and powdered, Vanadium pentoxide gives yields of over 80 per cent. of theory, and induces reaction at least as rapidly as in the finely-divided form. According to U.S.P. 1458478 of 1923, Vanadium pentoxide is fused, poured into moulds, suddenly chilled, and the solid powdered or granulated. U.S.P. 1463206 of 1923 recommends the addition of kieselguhr before moulding and grinding. In either form, the powdered Vanadium pentoxide is mounted upon a surface, such as broken bricks or metal.

Sodium compounds reduce the activity of a Vanadium pentoxide catalyst. Sulphur dioxide or Arsenious oxide, either in the reacting gases or mixed with the catalyst, have no influence.

Molybdenum oxide may be prepared from Ammonium molybdate by heating, or from Molybdic acid. Prepared from Ammonium molybdate, the oxide is dark coloured, due to some reduction to a lower oxide by the action of hot Ammonia. The degree of activity of the Molybdic oxide is independent of the mode of preparation, its state of oxidation, or the presence or absence of a support. It has the disadvantage of being appreciably volatile at the temperature of reaction.

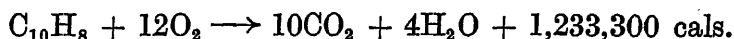
Kusama (*J. Chem. Soc. Japan*, 1923, 44, 605) has confirmed the work of Gibbs, and shown that a mixture of Vanadium pentoxide with a little Molybdic oxide gives especially good results.

Craver and the Barrett Co. (U.S.P. 1489741 of 1924) recommended a mixture of Vanadium pentoxide (65 per cent.), Molybdenum oxide (35 per cent.), with small quantities of either Manganese peroxide

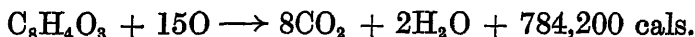
or Copper oxide. A temperature of 450° C. and a time of contact of half a second were mentioned for this catalyst.

Reaction. The production of Phthalic anhydride from Naphthalene is a strongly exothermic reaction, as the following thermochemical data show.

Heat of combustion of Naphthalene :—



Heat of combustion of Phthalic anhydride :—



Hence subtracting, we get for the heat of reaction :—



This quantity of heat is far in excess of that required to raise the temperature of Naphthalene vapour and the theoretical quantity of air, from the temperature of vaporisation of the former, up to the temperature of the reaction. With such a gas mixture, the catalyst would therefore soon fuse, unless means of cooling were employed. It is preferable to effect a thermal balance by using a very great excess of air—at least 10 times the theoretical quantity—when the reaction takes place smoothly, the product is purer and the yield better.

With a Vanadium pentoxide catalyst, the reaction commences at 270—280° C., and becomes rapid at 320—330° C. Decomposition or complete combustion does not become pronounced until temperatures above 400° C. are reached. Hence the range of temperature for a good yield is a wide one. Using Molybdenum oxide, a considerably higher temperature is necessary.

Kusama (*J. Chem. Soc.*, Japan, 1923, 44, 605) showed that the temperature of the catalyst is not uniform when the type of apparatus as described is employed. In a tube, the catalyst temperature rises to a maximum in passing along the tube, the position of this maximum depending upon the point where the reaction is completed. The course of the reaction can be followed by plotting the variation in temperature from one end of the tube to the other. A sharp maximum in the early part of the tube indicates that combustion is proceeding too quickly, and that much complete combustion is occurring. The speed of the reacting gases should then be increased, and adjusted so that the temperature rises gradually along the tube, attaining a maximum near the exhaust end. The reaction will then be proceeding smoothly, and a good yield of Phthalic anhydride result. The speed of the Naphthalene-air mixture should be as great as possible consistent with nearly complete conversion. This is very fast, although the rate of partial combustion of organic substances is never so great as, for example, the rate of oxidation of

Ammonia in contact with Platinum gauze. The proportion of air used does not matter so long as it is at least 10 times the amount required by theory. To obtain such a mixture, the temperature of the Naphthalene bath in the apparatus described should be between 90° C. and 130° C.

The chief solid product of the reaction is Phthalic anhydride. Other products that can be easily identified are α - or 1:4-Naphthoquinone and Benzoic acid. In addition, a small quantity of a volatile compound of sharp, irritating odour and pronounced lachrymatory properties is formed, and some brown, tarry, slightly volatile substance. The two latter bodies are formed more abundantly when the catalyst is old or working badly. α - and β -Naphthols are formed in minute quantities. Carbon dioxide is the main gaseous product. No Carbon monoxide is formed.

Phthalic anhydride made by the partial combustion of Naphthalene is easily separated from all bye-products by resublimation. Water (free, or combined as Phthalic acid), Naphthalene, and Benzoic acid distil first, followed by a sharp separation of the Phthalic anhydride, while the coloured material remains in the retort.

Gibbs (U.S.P. 1450678) obtained Phthalimide, or an alkyl derivative of Phthalimide, by passing Naphthalene vapour and air over a catalyst as described, and mixing Ammonia or a primary amine with the hot gases as they left the catalyst. Alternatively, the Ammonia or amine was mixed with the Naphthalene vapours and air.

Large quantities of Phthalic anhydride are now made by this reaction, in Germany, the United States, and by Scottish Dyes, Ltd., in Great Britain. A blower delivers a swift current of air over the surface of molten Naphthalene to a heat interchanger, where the mixture is preheated by the hot gases leaving the catalyst. The catalyst, consisting of fused Vanadium pentoxide, mounted on a suitable support, is better arranged in separate portions, or tiers, instead of in one continuous mass, and the connections to the reaction vessel are such that the Naphthalene-air mixture can be passed in either direction over the catalyst. A subsidiary cold air supply makes it possible to cool the catalyst rapidly, if necessary. By these arrangements, accurate temperature control of the catalyst is possible, and the reaction can be made almost completely autothermic.

The Partial Combustion of Tetrahydronaphthalene

Experiments with Tetrahydronaphthalene ("Tetraline") have been carried out by the author, who found that this compound behaved in the same way as Naphthalene. The same catalysts effected the reaction, which commenced at the same temperature. The yield of Phthalic anhydride was no greater than when Naphthalene was used.

The Partial Combustion of Toluene

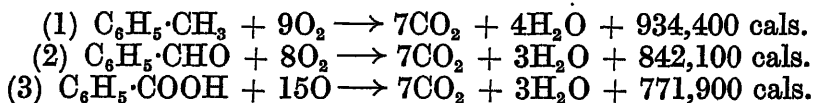
The possibility of obtaining Benzaldehyde and Benzoic acid from Toluene by catalytic oxidation has long been recognised, and several references, already given, are to be found in the literature. The first hint of a possible industrial process was contained in Walter's work, but searching investigations were first undertaken by Gibbs, and by Weiss and Downs. The following patents and papers have appeared: Chavy, Delage and Woog, F.P. 379715 of 1917. Other patents of about the same date mention the formation of Benzoic acid, but not of Benzaldehyde. Weiss and Downs, U.S.P. 1321959 of 1919; Gibbs and Conover, in patents and other announcements, already enumerated in connection with the partial combustion of Naphthalene; Selden Co., E.P. 170022 of 1920; Craver, E.P. 189091.

Apparatus. A modified form of the apparatus described in connection with the partial combustion of Naphthalene is suitable, as follows: Since a high proportion of Toluene is used in this reaction, a larger vaporiser is required, and the air current made to bubble through the heated liquid. On a large experimental scale it is preferable to drip, or spray, liquid Toluene at a measured rate into the air current (previously heated), since the air-toluene mixture necessary for the reaction is an inflammable one, and the space containing this explosive mixture can by this procedure be minimised. A very efficient coil condenser is necessary to collect the reaction products, followed by a scrubber containing a solvent for Toluene. Unless this is used, large quantities of unchanged Toluene escape with the exhaust gases.

Catalyst. The only useful catalysts hitherto found contain either Vanadium pentoxide or Molybdenum oxide. These can be made in either of the ways already described and are equally active in each case. The proportions of the products vary, however, according to whether Vanadium pentoxide or Molybdenum oxide is the catalyst. Numerous other oxides and mixtures give small quantities of Benzaldehyde, with larger quantities of Benzoic acid, which, if the catalyst is a basic oxide, tends to form a benzoate with it and reduce its further activity.

Craver and the Barrett Co. have proposed a mixture containing Uranium oxide (3 to 13 parts) and Molybdenum oxide (1 part). Another catalyst they have recommended contains oxides of Molybdenum, Uranium, and Copper.

Reaction. As the following equations shows the reaction is strongly exothermic:—



From (1) and (2) we obtain



From (1) and (3) we obtain



Control of the reaction is best maintained by using quantities of Toluene and air not far removed from the theoretical proportions for formation of Benzaldehyde, and adjusting the rate of flow of the Toluene and air mixture so that about 5 per cent. of the Toluene is converted at each passage over the catalyst. Under these conditions, equimolecular proportions of Toluene and Oxygen give a good yield, and the maximum rate of production, but a rather larger proportion of air—up to $2\frac{1}{2}$ times the theoretical quantity—has been recommended by Gibbs. A suitable mixture is obtained by passing the air-stream through liquid Toluene maintained at 60–100° C. This mixture is then passed over the catalyst at such a rate that the temperature of the catalyst rises to a maximum near the exhaust end. Using Vanadium pentoxide, this maximum should be between 350° C. and 450° C., and, using Molybdenum oxide, between 450° C. and 530° C. The proportions in which the products are formed are dependent upon the temperature of the catalyst, so that this maximum must be adjusted according to the products required.

Products of Catalytic Oxidation of Toluene. The three useful products are Benzaldehyde, Benzoic acid, and Anthraquinone. The proportion in which these three products occur is influenced by the temperature of the reaction, a high temperature being conducive to formation of Benzaldehyde. Since Molybdenum oxide requires a much higher temperature than Vanadium pentoxide, the products of reaction when this catalyst is used are those corresponding to a higher reaction temperature, viz., Benzaldehyde predominating.

Anthraquinone is never formed in quantities greater than 5 per cent. of theory of the Toluene undergoing conversion. None is formed at temperatures below 380° C. or above 500° C., using either catalyst. The greatest formation is at 420–450° C., using Vanadium pentoxide.

Using Vanadium pentoxide, the reaction between Toluene vapour and air commences at 280–300° C., but is very slow, and Benzoic acid is almost exclusively formed. At 350° C., reaction is faster, but Benzoic acid is still the main product. At 400–450° C., the reaction takes place at a speed convenient for obtaining a 5 per cent. conversion of Toluene per passage over the catalyst, and Benzaldehyde is the main product, being formed in quantities up to 50 per cent. of theory, calculated on the Toluene undergoing change.

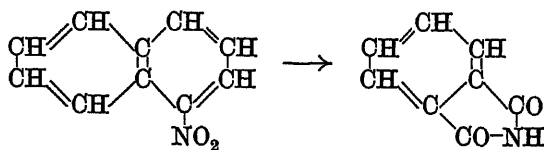
Using Molybdenum oxide, a temperature between 450° C. and

530° C. is necessary to obtain a suitable rate of reaction, and Benzaldehyde is always the main product, little Benzoic acid being formed. Small quantities of Anthraquinone are formed below 500° C., and considerable quantities of an oil, the proportion of which is greater as the temperature of reaction is increased. This oil boils over a wide range of temperature from 280° C. upwards. Its formation has not been mentioned by previous investigators, although at high temperatures it is found in considerable quantities—accounting for as much as 20 per cent. of the Toluene converted. With Vanadium pentoxide as catalyst, very little, if any, of this oil is produced.

Economic Possibilities. The partial combustion of Toluene has not yet been carried out on an industrial scale, notwithstanding the cheapness of the starting materials and the value of the products obtained. This is due to the following practical difficulties. (1) The mixture of Toluene and air necessary for the reaction is an inflammable one, so that very special precautions would be necessary to render large scale working safe. (2) Employing the experimental apparatus described, the condensed product consists of a dilute solution in Toluene of Benzaldehyde, Benzoic acid, and Anthraquinone, while the amount of Toluene caught by the scrubber is almost as great as the amount of Toluene converted. For an economical process, it is therefore clear that a circulation over the catalyst would be necessary, circulating the reaction mixture at such a rate that a 5 per cent. conversion occurred at each contact, and scrubbing out the products of reaction by means of warm Toluene between each passage. Provision for maintaining Oxygen in the circulation would be necessary, and also an exhaust to the exterior through a condenser, and scrubber.

The Partial Combustion of α -Nitronaphthalene

The oxidation of α -Nitronaphthalene by ordinary chemical agents such as Chromic acid is well known, and leads to formation of Nitrophthalic acid (Beilstein and Kurbatov, *Ann.*, 1880, 202, 218). If, however, the oxidation is carried out in the vapour state with air, in the presence of a catalyst, the reaction takes an entirely different course. At 350° C., the Nitro-group participates in the oxidation, and the molecule of α -Nitronaphthalene is resolved into Phthalimide (British Dyestuffs Corporation, A. G. Green and Stanley J. Green, E.P. 183044 of 1921):—



This reaction illustrates the effect of temperature and the presence of specific catalysts on the stability of organic compounds.

Catalyst. Either Vanadium pentoxide or Molybdenum oxide, and either mode of preparation as described in connection with Phthalic anhydride, can be employed. In E.P. 183044 it is recommended to mount the catalyst on pumice, by evaporating with a water solution of Ammonium vanadate or Ammonium molybdate, and heating the impregnated pumice until Ammonia ceases to be evolved. The amount of catalyst should be 15 to 25 per cent. by weight of the pumice.

Reaction. Air, filtered through cotton wool, is passed at a measured rate over the surface of melted α -Nitronaphthalene, maintained at a steady temperature (130 – 170° C.), and thence through a tube containing the heated catalyst to the condenser. An excess of air, at least 10 times that required by theory, is necessary.

The reaction commences at a temperature of about 300° C., using Vanadium pentoxide, and becomes rapid at 330 – 350° C. The best working range is 330 – 370° C. Using Molybdenum oxide, the reaction temperature is higher.

Products of Catalytic Oxidation of α -Nitronaphthalene. The main product is Phthalimide in a highly pure state, melting point 228° C., the yield being 40–50 per cent. of that theoretically possible. In addition, Phthalic anhydride is formed in amount equivalent to an addition of 15–20 per cent. to the yield. The two products condense separately from one another, owing to their widely different volatilities. The Phthalimide crystallises first, and then the Phthalic anhydride at a point considerably removed. Purification of the two substances by resublimation is easy.

This reaction has not yet been applied technically, owing to the superior economy of the Naphthalene to Phthalic anhydride oxidation.

The Partial Combustion of Anthracene

The oxidation of Anthracene to Anthraquinone by air, in presence of Vanadium pentoxide, was noticed by Walter (*J. pr. Chem.*, 1892, 46, 107), but the first important investigations were carried out by Gibbs and Conover, who protected the reaction in U.S.P. 1417367. More recently, Senseman and Nelson have given a detailed account of their work on this subject (*J. Ind. Eng. Chem.*, 1923, 15, 521).

Apparatus. The apparatus already described is suitable, with modifications necessitated by the lower volatility of the starting material and of the product. The vaporiser, a large, shallow, enclosed pan, exposes a wide area of melted Anthracene to the passing air, which has a direct passage over the Anthracene to the reaction chamber, through wide heated tubes, which are kept as short as possible. The reaction tube is electrically heated, but not branched,

provision being made at the inlet end for the insertion of tubes carrying pyrometer wires. At the exhaust end is attached a sublimation chamber, which can conveniently consist of a fairly large canister fitted or cemented (*e.g.*, with water glass and powdered asbestos) directly to the end of the reaction tube.

Catalyst. Vanadium pentoxide is the best catalyst, and it can be made by either of the methods already described.

According to Senseman and Nelson, when in its most active state the catalyst contains lower oxides of Vanadium as well as the pentoxide. They also adduced evidence which indicated that the mechanism of the reaction consisted in alternate reduction of the Vanadium pentoxide by Anthracene, forming Anthraquinone, and reoxidation of the lower oxides of Vanadium so formed by air. Thus, Anthracene and Vanadium pentoxide were enclosed in a sealed tube, evacuated to 2 mm. air pressure, and heated to 500° C. for 1 hour. The Vanadium pentoxide changed to a bluish-green solid, and 10–15 per cent. of the Anthracene had been oxidised to Anthraquinone.

The same investigators found that fresh brown Vanadium pentoxide gave only low yields of Anthraquinone, much unchanged Anthracene and a reddish-brown product being obtained. Such a catalyst tended, however, to improve with use. In their experiments, they placed Vanadic acid paste either on pumice, a glass tube which fitted inside the reaction chamber, or on perforated asbestos discs, and heated the Vanadium pentoxide to fusion in each case before use. The highest yields were obtained with the glass support.

Reaction. Using Vanadium pentoxide, the best results were obtained at a temperature of 400–420° C. If the temperature of the catalyst was appreciably below the boiling point of Anthraquinone, tarry material containing only a low percentage of Anthraquinone and unchanged Anthracene were mostly obtained. Above 425° C., the yield of Anthraquinone diminished owing to more complete combustion, but the product obtained was purer.

The best proportion of Anthracene to air was stated by Senseman and Nelson to be between 0.22 and 0.32 gram of Anthracene per litre of air, that is, an excess of Oxygen of 3 to 5 times that theoretically required for conversion into Anthraquinone. If the proportion of air was greater or less, the yield of Anthraquinone diminished. A rate of passage as great as possible, consistent with nearly complete conversion, was desirable. Under the best conditions a yield of 80 per cent. of that theoretically possible was obtained.

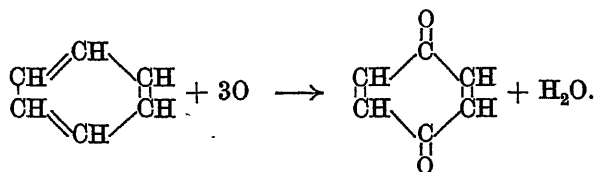
Partial Combustion of Other Organic Substances

Benzene. Weiss and Downs, in attempting to obtain Phenol by catalytic oxygenation of Benzene, found that small quantities only of this substance were obtainable, but that appreciable quantities

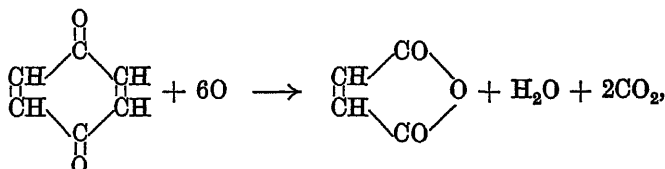
of Maleic acid were formed (*J. Ind. Eng. Chem.*, 1920, 12, 228). According to the method of U.S.P. 1318632 of 1919, a mixture of Benzene and Benzoquinone, in the vapour state, is oxidised under pressure by a gas containing Oxygen at a temperature between 300° C. and 700° C., in the presence of Vanadium pentoxide as catalyst. The Maleic acid formed is separated, and the residual Benzene and Benzoquinone are again subjected to the same treatment. According to U.S.Ps. 1318631 and 1318633 of 1919, Maleic acid and Benzoquinone are obtainable when Benzene and air are passed over a suitable catalyst at 300–500° C.

Weiss and Downs regard the oxidation of Benzene as taking the following course:—

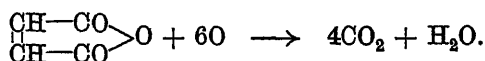
Benzoquinone is first formed,



On further oxidation, Maleic anhydride is formed,



but the oxidation is prone to go to completion,



so that yields of Maleic acid are not high.

Xylene. Gibbs and Conover, in the patents already referred to, state that Xylene vapour and air, with a suitable catalyst (V_2O_5), produce a mixture of Methyl benzaldehydes, Phthalaldehydes, Benzene dicarboxylic acids, Toluic acids, Benzoic acid, and Benzaldehyde.

Ortho Cresol. Weiss and Downs, U.S.P. 1380277, state that ortho-Cresol gives a mixture of Salicylaldehyde and Salicylic acid when passed with air over a suitable metallic oxide catalyst.

Fluorene. Weiss and Downs, U.S.Ps. 1374695, 1374720–2, of 1921, claim that Fluorenone is produced when Fluorene is passed with air over a suitable metallic oxide catalyst, at temperatures between 300° C. and 700° C.

Phenanthrene. Treated in the same way as Anthracene, which gives Anthraquinone, Phenanthrene produces Phenanthraquinone (Lewis and Gibbs, U.S.P. 1288431 of 1918).

Methane. The partial combustion of Methane to Formaldehyde has been effected on a laboratory scale, economical yields being obtained, but no results have been published. Work in this direction appears to have been discouraged by the development of the synthetic process for Methyl alcohol, the production of Formaldehyde from water gas, *via* Methyl alcohol, possessing superior advantages to the oxidation of Methane.

In a series of investigations on the partial combustion of organic substances, the present author found that: (1) The following oxides were so energetic that products of partial combustion could not be isolated in any quantity, the only stable products being Carbon dioxide and water: NiO , CoO , Fe_2O_3 , MnO_2 , Ag_2O , CuO , Cr_2O_3 , all prepared by precipitation. (2) These oxides were even more energetic in certain mixtures, especially when one was basic and the other very weakly acidic. (3) The activity of these oxides was much moderated by combination with a more strongly acidic oxide, such as As_2O_3 , P_2O_5 , MoO_3 , WO_3 , UO_3 , V_2O_5 , or B_2O_3 , so that using as catalysts Arsenites, Phosphates, etc., of the metals mentioned under (1), products of partial combustion could sometimes be obtained. The most valuable of these catalysts were Ferric compounds, especially Ferric tungstate, and it was shown by H. F. Oxley that a mixture of Methane and air when circulated rapidly over this catalyst at a high temperature gave Formaldehyde in an economical yield.

CHAPTER VI

NITRIC ACID

Introduction. Properties of the Oxides of Nitrogen. Ostwald's Process. Kaiser's Researches. Frank and Caro's Method. The German Process at Höchst. Development of the Process in (a) The United States, (b) Great Britain. Application of Ammonia Oxidation to the "Lead Chamber" Sulphuric Acid Process. Form of a Platinum Catalyst, and Effect of Foreign Substances. Non-platinum Catalysts. Maxted's Researches. Manufacture of Nitric Acid by Bayer und Co. at Leverkusen. Absorption of Oxides of Nitrogen. Bibliography.

FOR many years, the increasing demand for Ammonia, Ammonium compounds, Nitric acid, and Nitrates has threatened to overtake the natural sources of supply, and the fixation of atmospheric Nitrogen has been recognised as a chemical problem of prime importance. The final incentive came with the Great War, which led to an enormous concentration of research upon this problem in all the belligerent countries. Coal distillation as a source of Ammonia, and the Nitrate beds of Chile could no longer cope with the demands, and methods for combining atmospheric Nitrogen were rapidly worked out and exploited. Ammonia was synthesised chiefly by two methods: (1) From Cyanamide, but more especially by (2) the Haber process, and its later modifications. Nitric acid was obtained by (1) the Birkeland-Eyde method, by the direct union of atmospheric Nitrogen and Oxygen under the influence of the high temperature of an electric spark, and (2) the oxidation of Ammonia. In those countries short of water power, Ammonia oxidation became much the more important method, and enabled Germany to maintain the enormous supplies of nitro-explosives for the Central powers after the blockade deprived them of all external resources.

For some years after the conclusion of the armistice, research was energetically pursued in all countries, aiming at establishing industries profitable in peace, and capable of rapid reorganisation to the needs of war. Hence much attention was expended first on the production of synthetic Ammonia—a highly economic proposition—and secondly on the oxidation of Ammonia to Nitric acid. Ammonium salts in any quantity are always assured a ready outlet as fertilisers, hence the decision to make Ammonia the primary product of Nitrogen fixation, obtaining Nitric acid from this whenever, as in the event of war, increased supplies should be required.

Theoretical. Nitrogenous compounds generally, when mixed with air or Oxygen and passed over a catalyst at a suitable temperature, yield their Nitrogen mainly in the form of Nitric oxide. Moldenhauer and Wehrheim (*Z. angew. Chem.*, 1914, 27, 334) have shown that organic substances in which Nitrogen is linked to Carbon, more especially Cyanogen derivatives and nitriles, are burnt catalytically with greater ease than Ammonia, and frequently yield Nitric oxide under conditions which, in the case of Ammonia would give only Nitrogen.

The oxidation of Ammonia to oxides of Nitrogen was discovered as far back as 1839 by the French chemist Kuhlmann (*Ann.*, 1839, 29, 281), who showed that Platinum, as well as a number of other metallic and non-metallic substances, catalysed the reaction.

From the equation

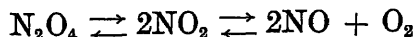


and the known properties of Nitric oxide, several important points can be deduced. Since the forward change in the reaction is exothermic, then, assuming it to be reversible, the highest conversion would be expected at the lowest possible working temperature. Application of the Nernst heat theorem shows, however, that at all practicable temperatures the equilibrium will approach very closely to complete conversion into Nitric oxide. Thus, from the equation

$$\log K_p = \frac{-Q_0}{4.571 T} + \sum \nu 1.75 \log T + \frac{\sum \nu \beta T}{4.571} + \sum \nu C$$

Anderson obtained values of K for temperatures between 500° and 1000° Abs., which showed in each case that with excess of Oxygen the reaction should proceed almost to completion.

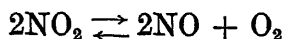
All the oxides of Nitrogen become unstable as the temperature is raised. The equilibria



shift rapidly with alteration of temperature. At the ordinary temperature the equilibrium is between N_2O_4 and NO_2 , and no Nitric oxide is present, but as the temperature is raised greater dissociation, first of N_2O_4 into NO_2 and then of NO_2 into Nitric oxide and Oxygen, occurs. Just above 600° C. dissociation of Nitrogen peroxide is complete. The Nitrogen oxide in the hot reaction product from Ammonia oxidation, immediately after it leaves the catalyst, will therefore be solely Nitric oxide, and this is confirmed by the fact that the gases are quite colourless until they have been cooled. If this cooling is carried out rapidly and efficiently it is possible to condense most of the water formed in the reaction before the Nitric

oxide has had time to oxidise, and the condensate is but faintly acid. This procedure is generally adopted on the large scale.

At higher temperatures, the equilibrium

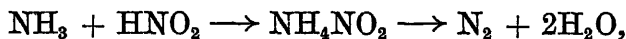


is complicated by the further change



which reaction is the basis of the Birkeland-Eyde method of manufacture of Nitric acid. Since Nitric oxide is an endothermic compound, being formed from its elements by absorption of heat, the equilibrium mixture between Nitrogen, Oxygen, and Nitric oxide will contain a greater percentage of Nitric oxide the higher the temperature. At the temperature of the electric arc Nitrogen and Oxygen combine to give a workable proportion of Nitric oxide in the resulting mixture. Nernst and Haber have found that, starting with air at 4140° C., equilibrium is attained with the formation of about 10 per cent. of Nitric oxide. At 2000° C. the equilibrium mixture contains not more than 1 per cent., while at the working temperature for oxidation of Ammonia this percentage is practically zero. Nitric oxide is therefore an unstable product, so that for a high efficiency the time of contact of the Ammonia-air mixture with the catalyst must be short, and the product of the reaction must be cooled as rapidly as possible to a point at which the velocity constants in the equilibrium $2\text{NO} \rightleftharpoons \text{N}_2 + \text{O}_2$ are small; that is, to a low red heat at least, assuming the complete exclusion of substances that can act as catalysts in this change.

Large losses of efficiency may also be brought about by incomplete reaction. Thus, if Ammonia escapes oxidation, this will later react with Nitrous acid in the product, eventually forming Nitrogen,



resulting in a loss of efficiency corresponding with double the amount of Ammonia unchanged. Conditions of working must therefore strike a compromise between the restrictions imposed by this cause of loss and that imposed by the conditions of stability of Nitric oxide. A fast gas current is necessary. To secure nearly complete conversion with a short time of contact with the catalyst, this must be in a condition of maximum activity, sufficient air must be used, and the gases preheated, and a temperature employed erring on the high rather than the low side.

Instead of the normal course, under certain conditions only the Hydrogen of the Ammonia may be oxidised.



This reaction, when a Platinum catalyst is used, is often accompanied by a "singing" Hydrogen flame. It is the predominant reaction in contact with some metal and oxide catalysts. Until recently, it was believed that a mixture of Ammonia and air at a high temperature was unstable, and tended even in the absence of any contact agent to react in this way. Taylor (*J. Ind. Eng. Chem.*, 1919, 11, 1121) has shown, however, that this is not the case, since in contact with firebrick, a 10 per cent. mixture of Ammonia in air is only very slowly altered even at 700° C.

With Platinum, under well-regulated conditions, oxidation of Ammonia yields Nitric oxide and water almost exclusively. The oxidation commences at a dull red heat, becomes rapid at 650° C., and proceeds without complication up to 900—950° C. The theoretical proportion of Ammonia to air is 1 : 6, but this leads to incomplete oxidation, Nitrogen and water being formed in considerable quantities. At least 1 : 7 is necessary, while actually the best results are obtained with the proportions about 1 : 9. Lower proportions of Ammonia than this are a disadvantage, on account of the cooling effect on the catalyst.

The first attempt at commercial exploitation was based on the researches of Ostwald, commencing in 1901, and protected by patents taken out in Great Britain (E.Ps. 698 and 8300 of 1902), France (F.P. 317544), United States (U.S.P. 858904), and Switzerland. In Germany, patent protection was denied owing to the previous work of Kuhlmann, and the process was developed secretly. By 1909, a small plant was in operation at Gerthe, in Westphalia, and probably continued working up to the commencement of the war. Shortly after, an English Company erected plant at Vilvorde in Belgium, and the results obtained probably furnished the details given in the first published account of large-scale workings (*Iron and Coal Trades Review*, May 23rd, 1913). This plant was captured early in the war by the Germans, but there is no evidence that they ever worked the Ostwald process on a large scale, either at Gerthe or Vilvorde.

Plant similar to that at Vilvorde was then erected during the war at Angoulême in France and Dagenham in England.

The Ostwald Process. Mixed Ammonia and air, containing 5 to 8 per cent. of the former, pass through a long outer tube, and are preheated by contact with an inner coaxial Nickel tube containing the catalyst at one end. This consists of a roll of corrugated Platinum foil, activated by a deposit of Platinum-black or Platinum sponge upon its surface. This roll is about 2 cm. deep, weighs about 50 grams, and fits loosely into the end of the Nickel tube, which is about 80 inches long and 2½ inches internal diameter. The reaction tube thus serves as a heat interchanger, gases leaving the catalyst traversing a considerable distance, during which they preheat the incoming

gases to about 650°C . The catalyst is maintained at upwards of 650°C ., the heat of reaction being sufficient to render the process autothermic. The effluent gases, consisting of Nitric oxide, Nitrogen, and Oxygen, are cooled, the Nitric oxide is allowed to oxidise (more air being added if necessary), and the resulting Nitrogen peroxide passed to absorbing towers (Fig. 3).

Nickel is not the best possible material for the reaction tube, since above 500°C . it exerts some destructive catalytic action. Aluminium or Silica is preferable, and these materials have more recently been used. The outer tube can consist of Iron, enamelled on the inside.

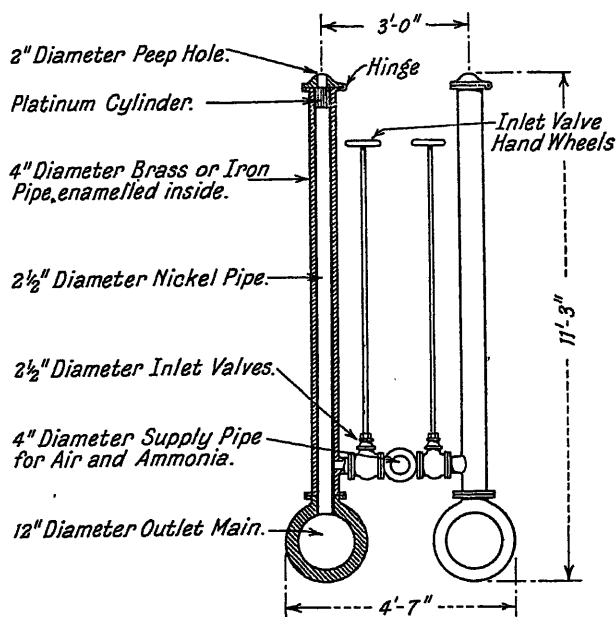


FIG. 3.—A double Ostwald unit.

Full details of attempts to work the Ostwald process have been published by Landis (*Chem. and Met. Eng.*, 1919, 20, 471). The plant at Angoulême was the most successful, and produced some thousands of tons of Nitric acid during the war. Its efficiency for a long time was reduced by the presence of Phosphine in the Ammonia, which poisoned the Platinum, but as soon as this cause was discovered and eliminated, 90 per cent. efficiencies were obtained.

The great disadvantages of the Ostwald process were: 1. The large amount of Platinum required (50 grams produced Nitric acid at the rate of 20 to 30 tons per year). 2. Temperature control of the catalyst was difficult. 3. The surface of catalyst exposed was not large, so that the concentration of Ammonia in the reacting gases could only be small, and the period of contract relatively long.

In each of these respects, the plant was improved by Frank and Caro.

Kaiser's Researches. In 1911, Kaiser of Heidelberg brought out the first of a series of patents, making striking claims for a process of Ammonia oxidation which he had developed (E.Ps. 24035 and 435397; U.S.P. 987375 of 1911). In 1912 a small plant was in operation at Spandau, near Berlin.

The efficiencies exceeding 100 per cent. which Kaiser at first claimed, and supposed were due to simultaneous autoxidation of the air used in the reaction, were soon proved fallacious, and due either to faulty methods of analysis or to the necessity of advancing some such novelty in order to evade technicalities of the patent law.

In this process the Ammonia-air mixture was preheated by mixing Ammonia with hot air in an Iron pipe immediately before it reached the catalyst. By this procedure the decomposition of the gases which occurred when they were passed through hot Iron pipes was largely avoided. The catalyst consisted of four separate layers of gauze composed of Platinum, or of Platinum alloyed with small quantities of Palladium or Iridium—the total thickness being about 0.5 mm. Kaiser appears to have been the first to employ Platinum in the form of gauze. Multiple gauze catalysts have been used almost exclusively since, and it has often been confirmed that a number of fine gauzes permits a much greater rate of flow than a single one, giving at the same time higher conversions and yields.

With modifications, the process has been applied commercially. For example, at Kharkoff (Russia), Saposhnikov claimed that an overall efficiency of 92 per cent. was obtained on the large scale. In many places, in England and elsewhere, this form of apparatus has been installed to supply Nitric oxide to the chamber plant in the manufacture of Sulphuric acid, and efficiencies of upwards of 90 per cent. have been obtained. For purposes of manufacture of Nitric acid, this method has, however, been superseded. A critical discussion of Kaiser's process is given in *Chem. Zeit.*, 1916, page 14.

✓|| *Frank and Caro's Method.* The great development in Germany, during the war, of Ammonia oxidation as a means of making Nitric acid on a large scale, was based on the method of Frank and Caro. This process (see D.R.-P. 234329) combines all the good points of the older ones. In spite of the war, and the importance attaching to this process as a means of making one of the chief munitions, a detailed account was published by Schuphaus (*Metall. u. Erz*, 1916, (2), 13, 22; *Chem. and Met. Eng.*, 1916, 14, 425) describing not only the first type of plant employed, but also the mode of operation. Later plants differed only in details of size, the substitution of multiple for single gauzes, and the abandonment of electrical heating.

Frank and Caro's earlier type of converter consisted of a short rectangular column, containing baffle plates, closed at the top by a conical hood, all composed of rolled Aluminium. The catalyst was fine Platinum gauze (80 meshes per linear inch, wire 0.0026 inch diameter), mounted across the rectangular column after the baffles and maintained electrically at a temperature of at least 650–750° C. by current conducted to it *via* silver leads. The gas mixture with this type of converter could be made considerably richer in Ammonia (about 10 per cent.), especially when, as later, multiple gauzes were substituted. The efficiency rose to 92 per cent., with an output of about $\frac{3}{4}$ ton of Nitric acid per 24 hours per square foot of catalyst surface.

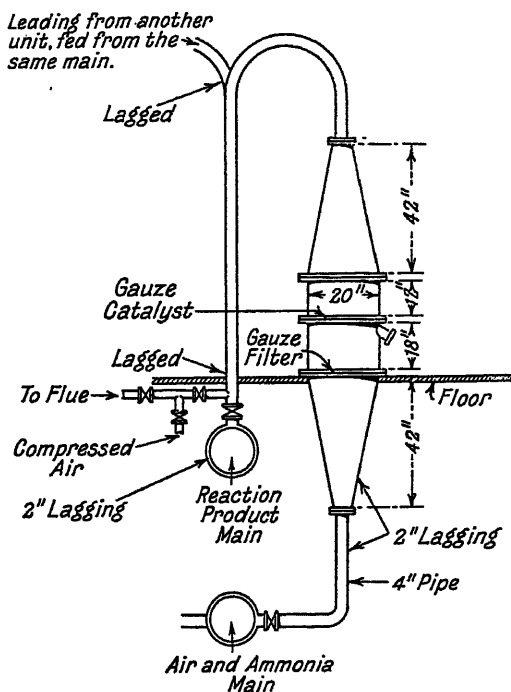


FIG. 4.

Large experimental units of this type were erected in America early in 1916, and, later, Nitric acid plant with a calculated output of 90,000 tons of Nitric acid per annum. Details of this are given by Pranke (*Chem. and Met. Eng.*, 1918, 19, 396) and Fairlee (*ibid.*, 1919, 20, 6). In Germany, the development of the Frank and Caro process supplied all the Nitric acid used for nitro-explosives in the later years of the war. The following is a description of the plant as finally elaborated at the Höchst Works of Meister, Lucius, und Brüning

(Partington, *J. Soc. Chem. Ind.*, 1921, 40, 185R).

Air and Ammonia, both carefully freed from dust by repeated filtration through layers of filter-cloth, were drawn through venturi meters into a centrifugal blower. The proportion of Ammonia, as indicated by the meters, was maintained at 12.5 per cent., within very narrow limits. The blower delivered the gases into a wide main, which conveyed them, first to a vertical lagged multitubular preheater, 15 feet by 5 feet external dimensions, heated by steam, and then to a heat exchanger of the same size and form, through which the incoming mixture passed counter current to the hot gases leaving the converters. Without the previous preheating with steam, acid tended to condense

in the exchanger from the converter product. After the double preheating, the gas mixture, now about 200°C ., passed through a wide lagged main which supplied a set of converters. These were made of cast Iron, and of two types.

In one type, the body of the converter consisted of four sections, flanged at both ends to enable them to be bolted together. The two middle sections, 18 and 12 inches high, respectively, and 20 inches internal diameter, supported the catalyst between them. The top and bottom sections were conical, each 42 inches high, and tapered to 4 inches internal diameter where they were bolted to inlet and outlet pipes of the same bore (Fig. 4).

The preheated gas mixture passed from the main, upwards through the converters arranged "in parallel" past the catalyst, which was maintained by the heat of reaction at about 800°C ., and out through a 4-inch tube bent into a semicircle. Heat expansion in the apparatus was taken up in the semicircular bend, which was the only part of the whole converter to be unlagged. It led to the outlet mains, common to the set of converters, which, in turn, led to the heat interchanger, and then to coolers. The gas mixture in the inlet main was under 6 inches of water pressure, and gate valves regulated its admission to the converters. A small air pressure was maintained on the outside of each gate valve to prevent leakage outwards. Each converter was provided with sight glasses, sampling tubes, a subsidiary air supply, and a bye-pass to the chimney. During normal working, the gases left the converter at $650\text{--}700^{\circ}\text{C}$., and a second type of converter was designed to enable this heat to be utilised (Fig. 5).

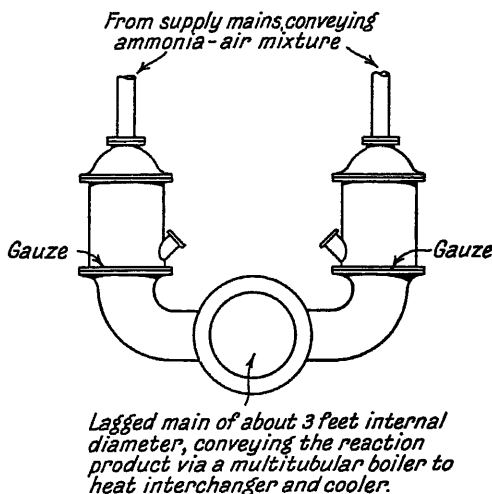


FIG. 5.

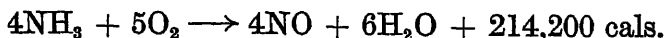
This type of converter consisted of a flanged cast Iron cylinder of about 2 feet diameter. The Ammonia-air mixture was led in from the main through the top, which was bell-shaped, and bolted to the top of the converter. The Platinum gauze catalyst was mounted at the bottom, and the gases after passing it were conveyed directly through an internally lagged pipe, almost as wide as the converter itself, to the exit main, also lagged internally, and which was common to a whole set of converters. This main led

the gases to the tubes of a multitubular boiler, where a large proportion of their heat was absorbed, the steam produced being used in the preheaters. Fifty-six converters, discharging their product through a boiler, evaporated 4 tons of water per hour, and the gases left the boiler tubes at a temperature of about 270° C. The gases were then passed on to a heat interchanger, and then to coolers as before.

The catalyst in each type of converter consisted of a plate of Platinum wire gauze, 20 inches in diameter, area 2.18 square feet. The wire was 0.06 inch in diameter, and was woven with 80 meshes to the linear inch, or about 1000 meshes per square centimetre. Three layers of this gauze were used in each converter, these layers being held close together by spot welding to a Platinum grid, and kept in place by embedding in asbestos. The total weight of catalyst per converter was 333 grams.

The life of a catalyst in this form was very long, the activity being unimpaired after 6 months' continuous working, so long as the conditions were uniform and the gases free from poisons. Gaseous friction was said to wear the gauzes if too fast a current was passed.

When oxidation was proceeding satisfactorily, the converters worked quite silently. Sometimes, however, a "singing" gauze was obtained. This usually indicated that oxidation was taking a wrong course (see Baumann, *Chem. Zeit.*, 1920, 44, 145). Thus, two reactions are possible, viz. :



which is the desired one, and



The second is the more strongly exothermic reaction, and an excessively high temperature beyond the contact zone indicated that this was occurring. The combustion of the Hydrogen, producing a Hydrogen flame, was often the cause of "singing," and the yield of Nitric oxide was found in practice to diminish with increasing pitch of the note sounded.

The reaction was started by applying a Hydrogen or a non-luminous coal gas flame to the catalyst, then turning on the Ammonia-air mixture. The heat of reaction quickly raised the gauze to its working temperature. Until the gauze had become activated and the converter reached its normal working temperature, the product was passed *via* a flue to the chimney. The temperature of the catalyst for satisfactory working was estimated at about 700° C., but in view of more recent and careful temperature measurements

carried out by United States investigators it is probable that this estimate is low. Certainly a much higher temperature does not vitiate the yield.

One square foot of catalyst, used as described, converted up to 20 lb. of Ammonia per hour, with an efficiency of 89 per cent.

Simultaneously with research and large-scale application in Germany, experimental research was being conducted in Great Britain by the Munitions Inventions Department of the Ministry of Munitions, and in America by the Bureau of Mines, in co-operation with the Semet-Solvay Company, under the direction of C. L. Parsons and L. C. Jones.

Development of the Process in the United States. Using a flat multiple gauze, and no external source of heat, it was found that heat was carried away too rapidly from the catalyst, with the result that either the rate of production or the efficiency fell below the maximum possible. A temperature sustained well above 750°C ., and preferably at $800\text{--}900^{\circ}\text{C}$., was shown to be necessary for a good conversion and high yield. The design of converter therefore aimed at conserving a greater proportion of the heat of reaction than was possible with a simple multiple gauze, and this was achieved as follows (Fig. 6): The Platinum gauze, of four superimposed layers, was bent into cylindrical form, and arranged so that the inside surface reflected against another red hot surface, while the outside received radiant heat from the firebrick lining of the converter, which soon attained a high temperature. With this type of apparatus and pure Ammonia, this converter remained entirely self-sustaining without preheating of the gases, though a heat regenerator, easily added, was later recommended for emergency use.

Aluminium pipes conducted the hot gases to the converter, contact with all other metals being avoided. After the converter,

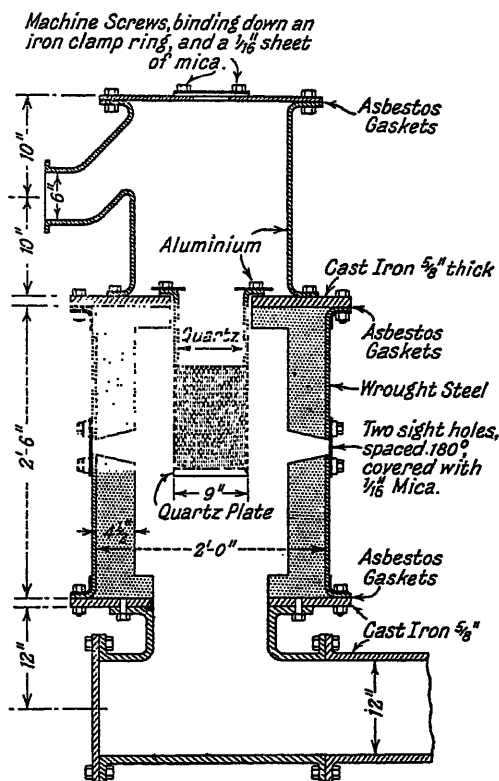


FIG. 6.

Iron pipes were used, but Iron was replaced by acid-resisting metal, or earthenware as soon as the temperature of the gases fell to 170–200° C., since at lower temperatures Iron was corroded. The converter itself was constructed of cast iron or boiler plating, lined inside with firebrick. The gases first passed into the Aluminium entrance chamber at the top, the capacity of which helped to absorb pulsations in the speed of the gas. After passing through the gauze cylinder, placed within the firebrick-lined converter, the gases emerged into the cast Iron chamber below, at a temperature of about 600° C. After passing a heat interchanger the gases were led to coolers, and then to an elaborate system of acid absorbers.

Windows covered with mica, in the top of the Aluminium entrance cap and in the body of the converter, enabled all parts of the interior to be viewed.

The gauze cylinder composing the catalyst was made by rolling a piece of activated Platinum wire gauze (80 mesh, 0.0026-inch wire), 13 inches wide and 113½ inches long, into a tube 9 inches wide. The walls of the cylinder so formed consisted of four thicknesses of gauze, of weight 16½ ounces. Unless the gauze is first activated (see later) by heating in a mixture of Ammonia and air, its activity never reaches the highest degree possible. Attempts to activate *in situ* result in the interior surface becoming highly active, while the outer layers of the gauze, more remote from the gas mixture, become active very slowly, or not at all. The catalytic surface was attached by Platinum wires to an entrance cylinder of Nickel or Silica, of the same diameter, and the other end of the gauze cylinder was closed by a Nickel or Silica plate. Silica or silicates are preferable to any metal, since even the most satisfactory of these, Nickel or Aluminium, have some tendency to catalyse the combustion of Ammonia to Nitrogen and water. Aluminium is better than Nickel in this respect, but its low melting point, about 650° C., precludes its use as part of the catalyst.

The reaction was started by applying a torch for a short time to the gauze, through one of the windows. On passing the Ammonia-air mixture, the reaction then started at once, and after a few hours, when the temperature of the whole converter had become steady, production of Nitric oxide took place regularly without interruption for many months.

It is probable that this type of converter (protected by U.S.P. 1321376, Parsons and Jones) is the most satisfactory hitherto devised, being cheap in construction and operation, giving a high efficiency and a large output for its size. The optimum rate of gas flow is about 200 cubic feet per minute, the Ammonia content being 10–11 per cent. The efficiency then reaches 94 per cent., and the capacity 200–210 lb. of 100 per cent. Nitric acid per hour,

or 21.7 lb. per square foot of catalyst surface. This efficiency is distinctly greater than that obtained at Höchst, and is due to the better heat conservation. By increasing the gas flow the rate of production can be raised to 250 lb. of Nitric acid per hour, but the efficiency then falls below 90 per cent. (Parsons, *J. Ind. Eng. Chem.*, 1919, 11, 541).

Careful observations of the gauze, when working under the optimum conditions, viz., a current of gas mixture of 200 cubic feet per minute, containing 11 per cent. of Ammonia, showed that its temperature was about 825°C . Lower temperatures gave smaller conversions and lower efficiencies. The temperature of a Platinum catalyst must on no account fall below 750°C . On the other hand, the efficiency of the operation tended somewhat to improve as the temperature was increased above 825°C ., though but little, and did not diminish until $900\text{--}925^{\circ}\text{C}$. had been passed. Other American investigators, e.g., Taylor (*J. Ind. Eng. Chem.*, 1919, 11, 1121), confirm that the best temperature for a Platinum catalyst exceeds 800°C .

Research in Great Britain. The large-scale experimental work initiated in Great Britain during the war did not lead to any important manufacturing industry, owing to the greater advantages of obtaining Nitric acid by the old method, from Chili saltpetre. Ammonia oxidation plant has, however, been installed in many factories in which Sulphuric acid is made by the lead chamber process, to supply the oxides of Nitrogen required. A brief account of the investigations carried out under the auspices of the Ministry of Munitions is given by Partington (*J. Soc. Chem. Ind.*, 1918, 37, 337R) and the application of the method in the lead chamber Sulphuric acid process is described by Imison and Russell (*J. Soc. Chem. Ind.*, 1922, 41, 37T).

The converter devised by Partington and his co-workers consisted of three rectangular segments, with flanges at both ends to enable them to be bolted together. To the top and bottom of these body pieces pyramidal segments were bolted. The rectangular area exposed measured 4 inches by 6 inches, and between all the junctions except the uppermost perforated baffles were inserted to complete the mixing of the gases (Fig. 7).

The top junction, that between the upper pyramidal piece and the uppermost body segment, held the catalyst, which consisted of one or more gauzes of pure Platinum wire, 0.0025 inch diameter, woven with 80 meshes per linear inch, mounted in an Aluminium frame.

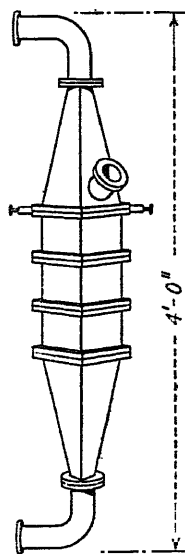


FIG. 7.

The converter was made entirely of cast aluminium $\frac{1}{8}$ inch thick. Each pyramidal segment tapered to a tube, 2 inches internal diameter, which was bolted to Aluminium tubes of the same bore. The overall length of the converter was about 4 feet, and its weight 32 lb.

Ammonia was injected through a nozzle into a stream of air from a blower, both gases being measured and then very efficiently mixed. In technical practice it was recommended to obtain the Ammonia from a strong aqueous solution, on account of its simplicity, purity, and convenience. This method was much used both in Germany and America, since in the synthetic process Ammonia was usually separated in the form of a 25 per cent. solution, while Ammonia from other sources was most readily purified from catalytic poisons by dissolving to a strong solution in water.

The mixed gases were then passed through fine coke packing, or glass wool, to remove dust and oxide of Iron, and led to the converter, which they entered at the bottom.

A mica window in the upper pyramid enabled the catalyst to be viewed during working, while an orifice in the top body segment allowed a non-luminous gas flame to be inserted to heat the gauze for starting the reaction. Alternatively, this may be effected electrically, as in the type of converter figured, where leads are shown. As soon as the Ammonia-air current was passed over the heated Platinum, reaction started, and the heat of reaction maintained the temperature. The reaction proceeded for several months without interruption, after which refitting with a new gauze was found necessary. Several gauzes in close proximity, as first described by Kaiser in 1910, were found to give better results than a single one. Thus, when a single gauze was used, and no heat supplied beyond that generated in the reaction, then a 90 per cent. efficiency could only be obtained with a gas flow corresponding with production of 0.25 ton of Nitric acid per square foot of catalytic area per 24 hours. With two gauzes under the same conditions, this could be raised to 0.35 ton (90 per cent. efficiency) or as much as 1.5 tons (85 per cent. efficiency). With four gauzes, 2 tons of Nitric acid could be obtained in the same time with an efficiency of 85 per cent. These figures show that for flow rates above a certain limit the efficiency tends to diminish. If, however, additional heat is supplied to the gauze, either by electrical heating or by preheating the entering gases to about 350° C., then the higher efficiency can be maintained for considerably greater rates of flow. The same point is illustrated by comparison between the results obtained by the German method (where no additional heat was supplied to the catalyst) and the American, where heat was conserved by the special construction of the converter.

The proportion of Ammonia to air may vary over wide limits

without affecting the efficiency of the process. Roughly, the limiting proportions for a good yield were found to lie between those theoretically required for the formation of N_2O_3 and N_2O_5 . The optimum proportion was approximately that which would correspond with formation ultimately of N_2O_3 , when the gauze was stated to attain a temperature of $650-700^\circ\text{C}$. When a mixture containing too much Ammonia was used, the gauze became overheated, leading to decomposition to Nitrogen, while with too low a proportion of Ammonia, unless extra heat was supplied, the catalyst did not become hot enough, in which case unoxidised Ammonia passed and loss again resulted.

Under the best conditions, the converter of design and size described produced regularly 1.5 tons of Nitric acid per square foot of catalyst area (that is, per 50 grams of Platinum) per 24 hours, with an efficiency of 95 per cent. This capacity and efficiency required preheating of the Ammonia-air mixture, or an external heat supply to the catalyst, without which the same output could only be obtained with an efficiency of 85 per cent. It is noted that the rate of production of a converter can be reduced to one-quarter of its maximum by reducing the rate of gas flow without reducing the efficiency.

Applications of the Ammonia-Oxidation Process

During the war the demand for Nitric acid was so great that to ensure supplies all the larger nations engaged devoted attention to this reaction. In 1918, Ammonia oxidation plants were in operation in Germany, the United States, France, Italy, and Russia. In Great Britain, the results of much experimental research were not developed on a large scale, since as a method of manufacture of Nitric acid the process is subject to several grave disadvantages. Thus, the absorption of acid from a rapid gas stream containing at most 10 per cent. of oxides of nitrogen requires either alkaline absorbents or else, if water is used, a very elaborate system of towers, practically doubling the capital cost of the plant. The use of alkalis is obviously uneconomical, unless nitrates, rather than the free acid, are required, while, using water, a stronger acid than 50 per cent. is very difficult to obtain. Although the concentration of 50 per cent. Nitric acid by means of vitriol is easy, the combined disadvantages of absorption and concentration render the process uneconomical, so long as supplies of mineral nitrate are forthcoming. The application of this process, at any rate in Great Britain, has therefore been confined to the production of oxides of Nitrogen for such purposes as the manufacture of Sulphuric acid by the lead chamber method, where difficulties of absorption and concentration do not arise. Most of the large Sulphuric acid works,

using the chamber process, have now installed units for the oxidation of Ammonia, with marked saving, at the same time reducing materially the quantity of 18,000 tons per annum of Sodium nitrate formerly imported.

Other advantages of Ammonia oxidation in conjunction with the lead chamber process are: (1) The oxides of Nitrogen are supplied regularly and unintermittently over long periods. (2) The working is almost automatic and clean compared with the "potting" of nitre. (3) The plant is very compact. An experimental unit with a gauze catalyst of 6 inches by 4 inches is sufficient to supply a chamber plant making 80 tons of Sulphuric acid per day.

The experimental units we have described have been modified to the needs of Sulphuric acid plant by Imison and Russell (*J. Soc. Chem. Ind.*, 1922, 41, 37T). These investigators confirmed that preheating of the gases is necessary for a high efficiency with a

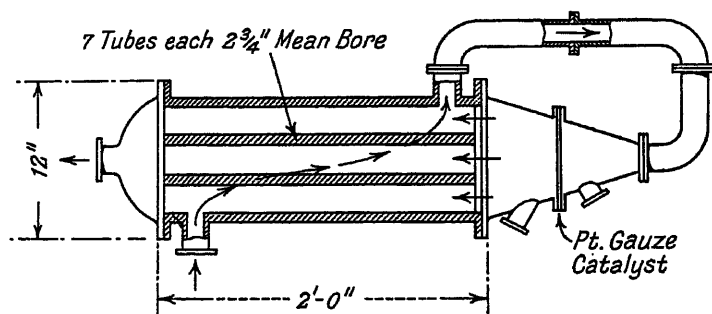


FIG. 8.

high rate of production, and ingeniously arranged their apparatus as follows: The contact vessel was funnel-shaped, and the wider end was bolted to the end of a multitubular heat-interchanger, the end plates of which were 12 inches across, and carried seven tubes, each 2 feet long and $2\frac{3}{4}$ inches mean internal diameter. The whole was made of cast Iron, enamelled on the interior, or painted over with "Sellars cement" (a mixture of Sodium silicate solution and Barium sulphate). The tubes and tube plates were cast in one piece, and the tubes tapered slightly for convenience in enamelling.

The Ammonia-air mixture first entered the spaces of the preheater, and emerged at about 300° C. through a pipe which bent round, and led to the narrow end of the converter. The gases passed the Platinum wire gauze catalyst, stretched across the wider end of the funnel-shaped converter, and were then delivered directly to the tubes of the preheater, where they gave up much of their heat to the incoming gases. After passing through several simple air-cooled silica coolers, the gases were taken directly to the chamber plant. Fig. 8 indicates the arrangement. The vertical position of

the gauze prevented sagging, and particles of Iron oxide from other parts of the converter could not drop on it.

A surface of 24 square inches of catalyst produced the equivalent of 50 cwt. of Sodium nitrate per week with an efficiency of 93 per cent. After 16 months' continuous working, the catalyst was still as active as formerly. The loss of Platinum varied between 0.002 and 0.004 troy ounce per ton of 100 per cent. Nitric acid produced.

Form of the Catalyst, and Effect of Foreign Substances

The multiple gauze Platinum wire catalyst has been used almost exclusively on the large scale, and appears to possess advantages over any other form. Palladium wire is more active than Platinum, but it rapidly falls to a powder, resembling Palladium-black. Pure Platinum has generally been used, but admixture of 1 per cent. of Iridium, or Palladium, as first suggested by Kaiser, does not in any way affect its catalytic action, and much increases the strength of the wire. With higher proportions of Palladium, the catalyst is much more difficult to activate, and it possesses no additional advantages.

With a view to determine the most suitable mesh and fineness of gauze, Campbell carried out a series of experiments, the results of which are recorded in *J. Ind. Eng. Chem.*, 1919, 11, 468. The figures indicated that the finest possible wire and mesh—giving a maximum exposed surface of metal—were desirable. Clearly a limit is set by the mechanical strength of the resulting gauze. When this was increased by alloying 1 per cent. of Iridium with the Platinum, it was considered practicable to employ 0.0015-inch wire, woven with 150 meshes per linear inch.

A clean and bright surface of metallic Platinum has a very low catalytic power, and must be activated before it can be used for oxidation of Ammonia. This is effected by exposing it to a current of pure Ammonia and air, at a temperature of about 800° C. Its activity gradually increases until at the end of several hours it has attained its maximum. This activation can be carried out *in situ* in the contact chamber, but for a multiple gauze catalyst it is generally preferable to use a special electrically heated apparatus, and a gas stream rather richer in Ammonia than that employed in the reaction. If only the heat of reaction is available, activation is slow, especially of those layers of gauze more remote from the fresh gas stream.

The active metal assumes a grey appearance, due apparently to a covering of spongy Platinum. Whether this covering merely increases the effective surface or in any way fundamentally alters it is uncertain. Microscopic examination shows that it has become

pitted and warted, leaving no suggestion of the original bright smooth surface. (See the photomicrograph in Imison and Russell's paper, *loc. cit.*)

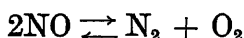
Platinum is also susceptible to the action of poisons. Iron and especially Iron oxide is a most serious impurity, 0.2 per cent. of Iron in the catalyst very seriously impairing its utility. Even the small amount added in drawing the wire with steel dies should be removed by boiling the gauze in strong Hydrochloric acid. Dust in the gas current is a very likely source of Iron contamination, and must be removed by filtration.

Sulphur, and sulphur-containing substances, and organic bodies which burn without residue, have no anticatalytic effect. Phosphine, or Acetylene, on the other hand, which are liable to be present in Ammonia obtained from Cyanamide, are generally supposed to exert a deleterious influence. According to Taylor and Capps (*J. Ind. Eng. Chem.*, 1918, 10, 457) as little as 2 parts of the former per 100 millions of mixed gases has a marked effect. Acetylene, 0.02 per cent., is serious, and causes a considerable fall of efficiency, while 0.1 per cent. lowers it to 65 per cent., or less. The effect of the Acetylene is visible, black, inactive patches appearing on the Platinum. Metal fouled with Acetylene in this way requires several hours' running with pure Ammonia and air to clean it. Similar black patches appear on the Platinum if grease, oil, tar, or various other organic materials are deposited on it. Gasworks Ammonia should therefore be purified by scrubbing in towers with strong caustic Soda solution (50° Tw.), and passing through charcoal purifiers. Nitrogen-containing bodies in the Ammonia are generally harmless, and often yield their Nitrogen as Nitric oxide more easily even than Ammonia.

More recently, Taylor and Capps have modified their earlier statement as to the poisonous effect of Acetylene (*J. Ind. Eng. Chem.*, 1919, 11, 27). Pure Acetylene, they now state, has no deleterious action and they attribute their earlier results to the presence of Phosphine. Perley also has found that Acetylene is not anticatalytic (*J. Ind. Eng. Chem.*, 1920, 12, 120), while Decarrière (*C.R.*, 1921, 172, 1663; 173, 148; *Mèin Poudres*, 1924, 21, 1, 68, 87, 106) reasserts that it is. Landis (American Electrochemical Society's meeting, April 3rd, 1919) has denied that Phosphine is harmful, and claims that Platinum activates itself to each gas mixture to which it is subjected, and a catalyst activated to crude autoclave gas will not work well with purified Ammonia, or coke-oven Ammonia, the period of adjustment from one quality of gas to another being 10 to 14 days. He also declares that there are structural differences in the form assumed by the metal activated to different qualities of gas.

Non-Platinum Catalysts

Many substances, including especially the oxides of the heavy metals, and combinations of these oxides with weak acids (Manganates, Plumbites, Chromates, etc.) facilitate the oxidation of Ammonia, and many patents have been taken out protecting their use. Claims also have been made for Silver and the metals of the Platinum group. It would appear that only those substances which catalyse the reaction



are precluded from possible use. Efficiencies of 90 per cent. appear to be realisable, at least on an experimental scale, with a number of different catalysts, but the rate of reaction is always much slower than when Platinum is used, so that considerably larger quantities are required.

Kuhlmann, who discovered the reaction in 1839, mentioned the oxides of Copper, Iron, and Nickel as catalysts. Du Motay (E.P. 491 of 1871) used Manganates, Permanganates, Bichromates, and Plumbites of the alkalis. Ostwald's patents protected the use of oxides of Manganese, Chromium, Lead, Silver, Copper, Iron, Nickel, Cobalt, Vanadium, Molybdenum, and Uranium, while Frank and Caro claimed the rare earths (D.R.-P. 234329). Very many recent patents reaffirm the catalytic properties of the oxides mentioned, and extend the list almost indefinitely. The following includes the substances which appear to have received most attention: Oxides of Silver, Chromium, Manganese, Iron, Cobalt, Nickel, Copper, the rare earths, and Bismuth, and Plumbites, Manganates, Chromates, Vanadates, Molybdates, Phosphates, and Aluminates of Zinc, Cadmium, Magnesium, Aluminium, and the Alkaline earths.

Goold, Adams, Partington, and Rideal overcame the mechanical difficulties in preparing oxide catalysts by forcing the partially dried gelatinous, precipitated hydroxide through orifices, and after completely drying, cutting into rods or threads (E.P. 126715 of 1917). They observed that Chromic oxide was most active when made by heating Ammonium chromate (E.P. 126716 of 1917), being comparatively inert when prepared by precipitation. They proposed to regulate the temperature of their catalysts by observing their luminosity and comparing with sources of light of standard intensity (E.P. 126717 of 1917).

Mixtures of oxides are frequently more active than either single individual constituent, and a number of clear instances of catalytic promotion have been established. The Badische D.R.-P. 301362 of 1915 mentions Copper oxide, with a subordinate quantity of a compound of Lead or Manganese. Most non-Platinum catalysts, however, consist of a basis of Iron oxide or Manganese oxide, with Bismuth

oxide or a rare earth (or both) as promoters. For example, Badische D.R.-P. 287009 of 1914 covers metals of the Iron group or their oxides, with Bismuth oxide or a rare earth. The rare earth can also replace the oxide of Iron, mixtures containing either Bismuth and rare earth, or Iron and rare earth being active catalysts. The Badische Norwegian Patent 26691 of 1916 and U.S.P. 1211394 also emphasise the usefulness of Bismuth oxide as a promoter, especially for the heavy metal oxides and rare earths.

Similar claims are made by U.S. Patents 1207706, 1207707, and 1207708. The first protects the use of mixtures of oxides of Bismuth, Iron, or Manganese, with Lanthana, Ceria, Ytria, Neodymia, or Praseodymia, and Lime, Magnesia, or Alumina as a binding agent. The second specifies particularly a mixture of Cerium and Bismuth oxides, while the third proposes Bismuth oxide mixed with either Iron or Manganese oxide. It is claimed that these catalysts, when bound into lumps, give 90 per cent. efficiencies and operate at 700°C .

An Iron catalyst, with and without various promoters, has been investigated by Maxted (*J. Soc. Chem. Ind.*, 1917, 36, 777). He showed that the efficiency of pure Iron was much increased by addition of Cerium, Thorium, Tungsten, Copper, and especially Bismuth. Alkalies like Potash had very little effect on the reaction, but Lime had a depressant action. Zinc and Manganese likewise exerted an unfavourable influence. The yields obtained, using different space velocities of the gas mixture, were expressed graphically, as follows:

(The temperature of the catalyst was 700°C .)

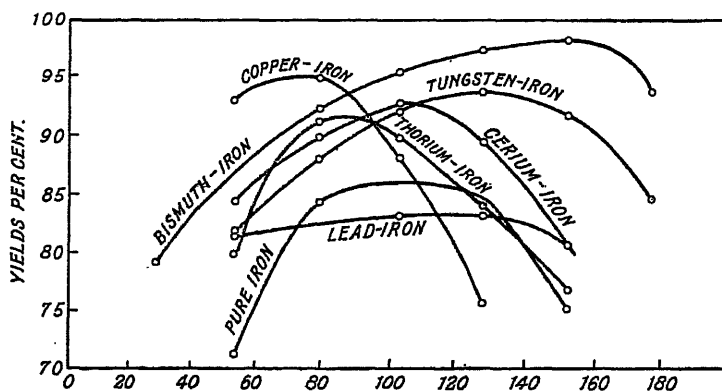


FIG. 9.—Velocity of passage of gas mixture in litres per hour (at room temperature) per c.c. of free space in the catalyst chamber. [Each c.c. of free space = 20 sq. metres of catalyst surface. A velocity of passage of 150 litres per hour corresponds with a time of contact of about 0.01 sec.]

From the graphs it will be seen that the time of contact for maximum efficiency varies according to the particular promoter present with

the Iron. Thus, Bismuth is the most active promoter, and gives a very high efficiency, with a time of contact of 0.01 sec. Cerium and Thorium mixtures require, respectively, 0.015 and 0.02 sec. for their highest yields. Lead exerts a curious influence, in that the efficiency becomes almost independent of the rate of passage.

In view of its relation to Bismuth, Antimony might be expected to promote the action. For a while it appeared to function, giving with a time of contact of 0.02 sec. an efficiency of over 90 per cent. After a short time, however, a graph was obtained corresponding with the one for pure Iron, from which it was concluded that the Antimony, in the form of its oxide, had vaporised from the seat of action.

Although high efficiencies can be obtained with catalysts other than Platinum, they have not been used on a manufacturing scale in any country except Germany. Even in Germany, in spite of the difficulty of supplies during the war, Platinum was more generally used. Its activity is so great that the quantity required, even for a big output, is small; its effective life is very long, and almost complete recovery from exhausted catalyst is easy. Procurability is therefore a more important consideration than price.

The advantage which the non-Platinum catalyst possesses in regard to original cost is more than offset by the fact that all are less active. For an equal rate of production, much more must therefore be used, with consequently larger and more expensive apparatus. The larger quantity of catalyst increases the difficulty of temperature control, so that in practice lower efficiencies are obtained than with the simple Platinum gauze.

The following is a description of plant used during the war at the Leverkusen works of Friedrich Bayer und Co. (*Chem. and Met. Eng.*, 1921, 24, 305, 347). ✓

Air was thoroughly filtered from dust by passage through layers of cloth, stretched across frames, and then delivered by a centrifugal blower to a cylindrical multitubular heat interchanger, 12 feet high and 12 feet in diameter, which it passed counterwise to the hot gases leaving the catalyst. After leaving the heat interchanger the air passed to a mixing vessel, in the shape of a truncated cone, about 3 feet long and 4 feet in diameter, arranged in an inclined position. The hot air entered the cone-shaped mixing vessel at the centre of its base, while Ammonia and cold air, the latter delivered through a bypass from the air blower, entered tangentially at the side. The Ammonia, not preheated, was maintained at about 7.5 per cent. of the mixture with the help of Venturi-meters. The mixture, at a temperature of about 360° C., then passed to the top of the converter, which it entered tangentially. The converter was cylindrical, about 15 feet high and 12 feet external diameter. Passing through it axially was a vertical tube, about 3 feet in diameter, along which a

current of cold air was blown by a fan. This helped to equalise the temperature in the catalyst bed (Fig. 10).

The hot gas mixture, entering the converter at the top, passed first through a perforated baffle, and then through the catalyst bed, which was about 6 inches deep and supported on a perforated plate about the middle of the converter. The area of the catalyst was about 5 square metres, corresponding with an internal diameter of 9 feet, and the pressure drop across the catalyst bed was about 10 centimetres of water. After starting the reaction, the heat generated maintained the temperature of the catalyst, and air cooling was necessary. For a high efficiency it is essential that the temperature of the catalyst should be uniform throughout the mass, since otherwise local action, leading to local overheating, takes place, with

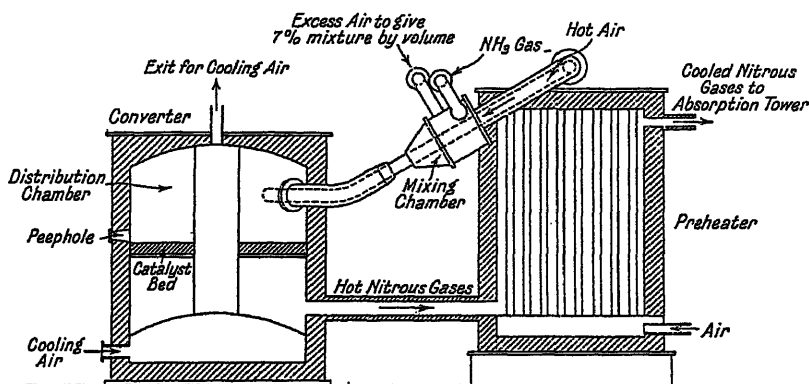


FIG. 10.

consequent decomposition. Within limits, the temperature of the catalyst does not affect the efficiency of the process, but it should lie between 700°C . and 850°C .

The lower part of the converter was empty, and the gases after passing the catalyst were conveyed directly through the heat exchanger to coolers and absorbers.

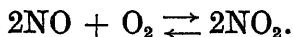
The exact composition of the catalyst was kept secret, but it consisted essentially of Iron oxide, and various promoters, probably oxides of Chromium and Manganese, agglomerated with Bismuth trichloride into granules of about 5 to 10 millimetres. A converter of the size and type described oxidised 5000 to 6000 kilos. of Ammonia per day, or 1100 kilos. per square metre of catalyst bed per day, with an overall efficiency of 80 to 85 per cent.

Absorption of Oxides of Nitrogen

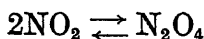
The absorption of oxides of Nitrogen from a rapid current of air was first investigated in connection with the Birkeland-Eyde method

of production of Nitric acid. In this process, the proportion of oxides of Nitrogen in the effluent gases from the arc is not more than about 1 per cent., and their complete absorption is a matter of great technical difficulty. To obtain Nitric acid from the product of oxidation of Ammonia presents similar difficulties, rather less serious, however, on account of the greater concentration of oxides of Nitrogen obtained. The gases leaving the contact chamber contain about 10 per cent. of Nitric oxide, which is oxidised to Nitric acid by the following series of reactions :—

1. Nitric oxide first combines with Oxygen (present in excess in the Ammonia-air mixture used, or added after the reaction to the cooled gases from the catalyst) to give Nitrogen peroxide. This is a "time" reaction, and reversible, and both the reaction velocity and position of equilibrium are much influenced by the temperature.



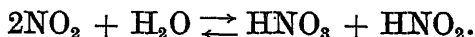
Thus, above 620° C., the Nitrogen peroxide is almost completely dissociated, while below 150° C. the Nitric oxide and Oxygen are almost completely combined. Below 100° C., the equilibrium



introduces a further complication.

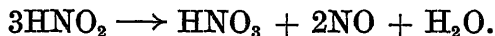
Raschig believed that Nitrous anhydride, N_2O_3 , was first formed during the oxidation of Nitric oxide, but Lunge and Berl (*Z. angew. Chem.*, 1916, 19, 807) showed that this was probably not the case.

2. The Nitrogen peroxide reacts with water, giving a solution containing equimolecular proportions of Nitric and Nitrous acids,



This action also is reversible, and requires time, but is fast at the ordinary temperature.

3. The Nitrous acid formed in the previous stage continuously decomposes into Nitric acid and Nitric oxide,



The latter then repeats the whole sequence of reactions.

This continual reproduction of Nitrous oxide, which takes place throughout the absorption system, renders complete absorption in water of oxides of Nitrogen from a rapid gas stream practically impossible. After absorbing as much as convenient in water, the remainder must therefore be recovered by use of some other solvent—generally an alkali.

Le Blanc (*Z. Elektrochem.*, 1906, 12, 541) showed that when an alkaline absorbent was used, the reaction



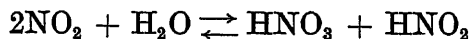
was almost quantitative, since immediately after absorption the solution contained equivalent proportions of nitrite and nitrate. In presence of excess of air, the former at once proceeded to oxidise to the latter.

The chief technical difficulty in the absorption of oxides of Nitrogen arises through the slowness of combination between Nitric oxide and Oxygen to give Nitrogen peroxide. A catalyst to increase the rate of this reaction would be of great value, and Chlorine or Bromine has been suggested for this purpose. The difficulty of subsequently removing these substances from the Nitric acid has, however, prevented their use. In practice, therefore, apparatus of sufficiently large capacity must be employed to enable the union of Nitric oxide and Oxygen to proceed to completion, even with a rapid gas current. Large capacity is necessary throughout the absorption system, since, as we have seen, Nitric oxide is continuously regenerated, and inefficient absorption must result if this is passed to an absorber before it has oxidised to Nitrogen peroxide.

Lunge and Berl (*Chem. Zeit.*, 1904, 28, 1243) found that the conversion of Nitric oxide into Nitric acid with excess of air was mainly influenced by the amount of water present. With the most favourable proportion almost complete conversion could be obtained. As the amount of water was increased beyond this, the proportion of Nitric oxide not oxidising beyond the Nitrous acid stage also increased. The reactions involved were gradual, and time was required for their completion. Lunge and Berl also found that strong Sulphuric acid was a useful absorbent for oxides of Nitrogen, since the compounds formed were stable except in the presence of water.

The behaviour of Nitrogen peroxide, when mixtures of this gas with Oxygen or air are passed through water, has been studied exhaustively by Foerster and Koch (*Z. angew. Chem.*, 1908, 21, 2161, 2209). The concentration of the Nitric acid formed depends mainly upon two factors.

1. The proportion of Nitrogen peroxide in the gas stream. Its partial pressure in the gas determines its concentration in the water, and therefore fixes the proportion of Nitric acid when the equilibrium



has been established. The concentration of Nitric acid will therefore tend to reach a limit, this limiting concentration being greater the higher the proportion of Nitrogen peroxide in the gas.

2. Evaporation of Nitric acid. The current of gas carries away Nitric acid vapour, the quantity evaporated depending upon the rate of the gas stream.

A current of Nitrogen peroxide and Oxygen, made by interaction of 1 volume of Nitric oxide with 2 volumes of Oxygen, was passed into water. Absorption and formation of Nitric acid were very rapid at first, until a solution containing 40 per cent. of acid was obtained. The speed then slackened, becoming still slower as the concentration of Nitric acid gradually increased. The reduced speed of reaction between Nitrogen peroxide and water was due to the lower active mass of the water, brought about by the formation of hydrates of Nitric acid. A concentration of 54 per cent. of Nitric acid was easily obtained, corresponding, it was noted, with the hydrate $\text{HNO}_3 \cdot 3\text{H}_2\text{O}$. From this point the action between Nitrogen peroxide and water was very slow. Raising the temperature still further reduced it, from which it was surmised that Nitric acid was formed from Nitrogen peroxide in the dimolecular form (N_2O_4).

Continued passage of the Nitrogen peroxide-Oxygen mixture produced a solution saturated with respect to Nitrogen peroxide, which was easily displaceable by boiling or by passing pure air. The concentration of Nitric acid rose very gradually to a maximum approaching 68 per cent. This concentration of acid corresponds with the mixture of Nitric acid and water of minimum vapour pressure, so that, as would be expected, evaporation prevents any further concentration however long the passage of the mixed gases is continued. Thus, beyond this concentration of Nitric acid, the vapour phase contains a higher proportion of Nitric acid to water than the liquid phase with which it is in equilibrium. Hence evaporation, either by direct distillation or by passage of a current of gas, reduces such a strength of acid until acid and water vaporise equally, that is, until the 68 per cent. strength is reached.

Since the absorption of the Nitrogen peroxide is very slow before this maximum concentration is reached, in practice it is very difficult to attain. If larger quantities of air or Oxygen are present, as is always the case in technical working, it is impossible. Thus, if a large proportion of air is present, evaporation of Nitric acid is proportional to the volume of air passing. At the same time, since the concentration of Nitrogen peroxide is lowered, the concentration of Nitric acid obtainable falls. Foerster and Koch determined the following limiting concentrations at the ordinary temperature: For 1, 2, and 5 per cent. mixtures of Nitrogen peroxide in air, the corresponding limiting concentrations of Nitric acid which could be obtained were 46, 52, and 55 per cent., respectively.

Factors governing the efficiency of absorption of gases in towers, with special reference to the case of oxides of Nitrogen in water,

have been investigated by Partington and Parker (*J. Soc. Chem. Ind.*, 1919, 38, 75T). The formation of a mist of aqueous Nitric acid, which may contain as much as 35 to 50 per cent. of acid, is an additional source of difficulty. A fine mist is very difficult to dissolve, and passes through water without sensible absorption or alteration in percentage of Nitric acid in the droplets composing it.

At the Höchst works of Meister, Lucius, und Brüning, where the possible annual output of Nitric acid amounted to 78,000 tons, the absorption plant was as follows: Of the total of 252 converters, the product from 224 discharged through 8 cast-iron mains, 18 inches in diameter, to the coolers and absorbers, which were arranged in four sets. The sets were similar in all essential points, each comprising 12 coolers, and 8 absorption towers, and dealing with the output from 56 converters. The hot gases from the 56 converters passed "in parallel" through the twelve coolers on their way to the first absorption tower. The coolers were made of Aluminium, and constructed so that the gases led in at the top, passed downwards through an annular space, both surfaces of which were cooled by running water. Each cooler was 5 feet high and $2\frac{1}{2}$ feet in diameter, and the cooling was so efficient that the gases left at 30° C. at the bottom, while the condensate, also run off at the bottom, was nearly free from acid. This was used to feed the fifth absorption tower.

The gases left the battery of coolers through 4 pottery mains, 1 foot in diameter, which united in a single brick chamber at the base of the first tower. Secondary air, to complete the oxidation of Nitric oxide, was added at this point.

Each absorption tower was 41 feet high and 21 feet in diameter (internally), built of three layers of brickwork, the outer being set in a mixture of Sodium silicate and kieselguhr. A central partition in each tower caused the gases to pass up one side and down the other, whence they passed to the next tower through a brickwork channel at the base. The towers were packed with stoneware, down which the absorbing liquid flowed, being fed by 8-inch chrome-steel centrifugal pumps. The pumps received their liquor through pottery mains, and delivered through Silicon-Iron pipes to the top of the towers, where the liquid was distributed by ribbed discs, rotating at about 80 r.p.m. The circulation of liquid in each tower was 110 gallons per minute, requiring two delivery pipes. Between the towers the acid liquid passed through water or ice-cooled S-pipes of Silicon-Iron, the absorption being better the cooler the absorbing liquid.

Acid of 50 per cent. strength was drawn off at the base of the first tower, and passed on to the concentration plant. Absorption was completed by use of a saturated Soda-ash solution in the last two (the 7th and 8th) towers of the series, and actually as much as

25 per cent. of the total output was recovered here in the form of Sodium nitrate. The Soda-ash solution in the first of these towers was allowed to become acid, so that all the nitrite decomposed, became oxidised, and was reabsorbed in the second tower, the contents of which were kept alkaline. The nitrate solution drawn off—nearly free from nitrite—was evaporated by waste heat from the converters.

The efficiency of the absorption was 97 per cent. As pointed out by Partington, the capacity of the absorbing system is only 81 cubic feet per lb. of Nitrogen peroxide absorbed per minute, this being much less than Partington and Parker (*loc. cit.*) calculated to be required, and far less than that employed at the French factory at Bassens, where 1500 cubic feet of space per lb. of Nitrogen peroxide absorbed per minute were allowed. This relatively small water-absorbing system at Höchst accounts for the considerable proportion of acid which remained to be absorbed by alkali.

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Japanese Patent : 1920, 35618.

CHAPTER VII

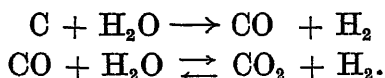
HYDROGEN AND HYDROGENATION

Introduction. The Manufacture of Hydrogen. 1. The "B.A.M.A.-G." Process. 2. The Griesheim-Elektron Process. 3. From Water Gas, by Liquefaction of the other Constituents. 4. By Decomposition of Water. 5. By Decomposition of Hydrocarbons. 6. By Electrolysis. 7. By Action of Metals on Acids. Hydrogenation. The Reaction of Sabatier and Senderens. Details of the Method: (a) Apparatus, (b) Catalysts: Nickel, Cobalt, the Platinum Metals, Iron, Copper. General Principles of the Reaction. The Observations of Moissan and Moureau. Action of Catalytic Metals on (a) Ethylene, (b) Acetylene. Cuprene. Hydrogenation of (a) Ethylene, (b) Acetylene. The Formation of Natural Petroleum. Hydrogenation of Ethylenic Compounds: (a) Hydrocarbons, (b) Alcohols, (c) Acids, (d) Esters, (e) Aldehydes, (f) Ketones, (g) Oxides. Hydrogenation of Acetylenic Compounds. Hydrogenation of Aromatic Compounds: (a) Hydrocarbons, (b) Aromatic Alcohols, (c) Aromatic Ethers, (d) Aromatic Acids, (e) Esters of Aromatic Acids, (f) Esters of Benzene-substituted Aliphatic Acids, (g) Aromatic Amines, (h) Benzene Substituted Aliphatic Amines, (i) Hydrogenation of Amines at High Temperatures, (j) Phenol, (k) Polyphenols. Hydrogenation of Polymethylene Compounds: (a) Cyclopropane, (b) Cyclobutane, (c) Cyclopentane and Cyclohexane, (d) Cycloheptane and Cyclo-octane. Hydrogenation of Fused Aromatic Nuclei: (a) Naphthalene, (b) Acenaphthene, (c) Fluorene, (d) Hydrindene, (e) Anthracene, (f) Phenanthrene. Hydrogenation of Heterocyclic Compounds: (a) Pyrrole, (b) Pyridine, (c) Indole, (d) Quinoline, (e) Acridine, (f) Carbazole, (g) Furane, (h) Ethylene Oxides. Reduction of Aldehydes. Reduction of Ketones: (a) Aliphatic, (b) Alicyclic, (c) Aliphatic Diketones, (d) Keto Acids and Esters, (e) Aliphatic—Aromatic Ketones, (f) Aromatic Diketones, (g) Aromatic—Aliphatic Diketones, (h) Quinones. Reduction of Acid Anhydrides. Hydrogenation of Nitriles: (a) Aliphatic, (b) Aromatic, (c) Dinitriles. Reduction of Oximes: (a) Aliphatic Aldoximes, (b) Aliphatic Ketoximes, (c) Cyclic Ketoximes, (d) Aromatic Aldoximes, (e) Aromatic Ketoximes. Reduction of: (a) Carbylamines, (b) Carbimides, (c) Amides, (d) Azobenzene and Phenyl Hydrazine, (e) Azines, (f) Hydrazones, (g) Schiff's Bases, (h) Oxides of Nitrogen, (i) Nitro-compounds, (j) Nitrous esters.

THE many uses of Hydrogen and the enormous quantities consumed have made it the most important of the industrial gases. Its applications are largely due to its properties of lightness, combustibility, and high heat of combustion, and the ability to enter into chemical combination which Hydrogen possesses in a degree not exceeded by any other element. For these reasons its use in aeronautics has been extensive; either free or combined, it forms a valuable constituent of fuel gases, and large quantities are required for chemical synthetic processes, such as the manufacture of Ammonia, Methyl alcohol, and catalytically hardened fats. Cheap manufacture of Hydrogen has therefore been a subject of much research, and many of the methods employed involve the catalytic principle. Since, however, information relating to these methods

is easily accessible in various treatises and other publications, only a brief summary, with the more important references, will be attempted here (see Greenwood, "Industrial Gases," London, 1919; Taylor, "Industrial Hydrogen"; and Rideal, *J. Soc. Chem. Ind.*, 1921, 40, 10r). The chief technical methods available for the production of Hydrogen are:—

1. The continuous catalytic process of the Badische Anilin- und Soda-Fabrik. This consists in preparation of water gas, and conversion of the Carbon monoxide present to an equivalent of Hydrogen, by passing the water gas with an excess of steam over a suitable catalyst,



This process, also described as the "B.A.M.A.-G." method (Berlin Anhaltische Maschinenbau Aktien-Gesellschaft), is the most economical known, and has now been adopted by the Badische Company to provide all the Hydrogen required for synthetic Ammonia. We shall describe this method in detail in that connection.

2. The Griesheim-Elektron process. Mertz and Weith (*Ber.*, 1880, 13, 718) and du Motay (U.S.P. 229339 of 1880) were the first to show that Carbon monoxide is almost completely replaced by Hydrogen when either pure Carbon monoxide or water gas is passed over slaked Lime at a temperature just below red heat. The Chemische Fabrik Griesheim-Elektron have elaborated this method, which is described in E.Ps. 2523 of 1909, 13049 of 1912, 7147 of 1913, D.R.-P. 284816 of 1914, and by Vignon, *Bull. Soc. chim.*, 1911, 9, 18.

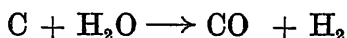
3. From water gas, or other technical mixtures rich in Hydrogen, by liquefying the more easily condensable constituents. This method was developed by Linde, Frank and Caro, who devised standard plant for the separation of Hydrogen from water gas, yielding a product containing as the only impurity a small percentage of Carbon monoxide. Gas made in this way is particularly suitable for catalytic purposes since (except for Carbon monoxide, which is easily removable) it is entirely free from anticatalytic substances, these being easily liquefiable, and soluble in liquid Carbon monoxide, condensation of which therefore exercises a scrubbing action. This method was formerly used by the Badische company for Hydrogen, in connection with synthetic Ammonia. (E.Ps. 4411 of 1892, 7205 and 9260 of 1911, 7147 of 1913, 13160 of 1914, and F.P. 445883 of 1912.)

4. Action of water or steam on elements which yield an oxide of high heat of formation. Technically, only Iron and Carbon are used, though many other elements react more easily and give a purer Hydrogen.

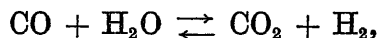
(a) Alternate action of steam and reducing gases on heated Iron

or Iron oxide. These reactions have been investigated by Deville (*C.R.*, 1870, 70, 1105, 1201); Debray (*ibid.*, 1879, 88, 1341); Preuner (*Z. Phys. Chem.*, 1904, 47, 385); Chaudron (*C.R.*, 1914, 159, 237), and Wöhler and Prager (*Z. Elektrochem.*, 1917, 23, 199). Originally, the steaming phase alone was proposed as a cheap source of Hydrogen. Later, the reduction phase in conjunction was suggested, using water gas, when it was discovered that at a high temperature, and in the presence of moisture, the Iron oxide was reduced exclusively by the Carbon monoxide. Surface contact action is here involved, and it is not unlikely that the preferential action, leading to the oxidation of the Carbon monoxide only, is due to the well-known tendency of Carbon monoxide to be adsorbed on oxide surfaces more easily than Hydrogen, thereby excluding this latter gas from reactions in which it would otherwise take part. Standard Hydrogen plants, working these reactions, have been used on a large scale and comprise the "Lane," and "Messerschmidt" processes. In essentials, the method consists in a separation into two stages of the B.A.M.A.-G. continuous catalytic process. (*J. Soc. Chem. Ind.*, 1916, 35, 1136; E. Ps. 593 of 1861, 2719 of 1865; 1471 of 1873, 20752 of 1890; 4134 of 1891; 21479 of 1908; 17591 of 1909; 11878 and 23418 of 1910; 6683, 12051, 12117, 12242, 12243, and 27735 of 1912; 17690, 17691, 17692, 18028, and 18942 of 1913; 16893 of 1914; 12698 of 1915; 119591 of 1918; D.R.-P. 232347 of 1910; 291603 of 1913, and 192902 of 1914.)

(b) Low temperature water gas formation, such as may be obtained by impregnating the carbon with a catalyst. The two stages of the water gas reaction then proceed together, viz.,



and



the equilibrium in which is less favourable to Hydrogen formation at higher temperatures (E.Ps. 7718, 7719, 7720, and 8734 of 1910).

(c) The Bergius process. This consists in acting on Iron or Carbon with liquid water. The temperature must therefore be brought below the critical point of the latter by use of catalysts. One of the advantages of the method is the fact that Hydrogen is delivered at high pressure. (E.Ps. 19002 and 19003 of 1912, D.R.-PP. 259030 of 1911, 262831 of 1912, 277501 and 286961 of 1913; *J. Soc. Chem. Ind.*, 1913, 32, 462; *Z. angew. Chem.*, 1913, I, 517.)

5. Decomposition of Hydrocarbons. Beyond a certain temperature, all hydrocarbons are "cracked" into Carbon and Hydrogen, this temperature depending on the stability of the particular hydrocarbon and the presence of catalytic surfaces. The Hydrogen formed is moderately pure, and the Carbon is deposited in a finely-divided state particularly suitable for the manufacture of water gas rich in

Hydrogen, since steam reacts with it at a comparatively low temperature. (E.Ps. 1466 of 1876; 2787 of 1880; 14601 of 1906; 15071 of 1909; 2298 and 24256 of 1910; 13397, 14703, and 16373 of 1911; 12978 of 1913; 2054 of 1914; 5098 of 1915; F.Ps. 391867 and 39168 of 1908; D.R.-PP. 229406 of 1909, 268291 of 1911; and U.S.P. 1092903 of 1914.) Using Acetylene, and decomposing it electrically, lampblack in a very finely divided form and pure Hydrogen are obtained.

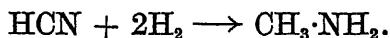
6. Electrolysis. As a method of manufacture of Hydrogen, electrolysis has been developed on a large scale where plentiful water power is available. In other cases, electrolytic Hydrogen can only be regarded as a bye-product in the manufacture of more valuable substances, as in the Castner-Kellner and other electrolytic processes.

7. Likewise when Hydrogen is made by the action of acids or alkalies on metals it can only be economical when other more valuable products are in the course of manufacture.

HYDROGENATION

THE REACTION OF SABATIER AND SENDERENS

Introduction. Prior to the researches of Sabatier, very few instances had been recorded of catalytic reduction by gaseous Hydrogen, or of direct addition of Hydrogen to unsaturated organic substances ("Hydrogenation"). Various catalytic reactions in which Hydrogen participated were discovered by Davy, Dobereiner, Faraday, and others, and have been described elsewhere, but these can hardly be classed as reductions or hydrogenations. The first catalytic reduction was discovered by Kuhlmann (*C.R.*, 1838, 17, 1107), who found that when oxides of Nitrogen were mixed with Hydrogen and exposed to the action of Platinum sponge Ammonia was formed. Debus effected the first catalytic hydrogenation (*Ann.*, 1863, 128, 200). By passing Hydrocyanic acid vapour mixed with Hydrogen over heated Platinum-black, Methylamine was formed,



In the same way, Debus reduced Ethyl nitrite to Ethyl alcohol and Ammonia,



and considerably later, using Platinum-black in the same way, Saytzeff reduced Nitrobenzene to Aniline (Kolbe, *J. pr. Chem.*, 1871, (2), 4, 418), Nitrophenol to Amidophenol, and Nitromethane to Methylamine (*ibid.*, 1873, 128). De Wilde then effected the hydro-

genation of Acetylene by passing it with Hydrogen over Platinum-black at the ordinary temperature, and obtained first Ethylene then Ethane,



Up to 1897, these few isolated and comparatively unimportant observations were the only known instances of catalytic hydrogenation and reduction. In that year Sabatier and his co-workers commenced one of the most remarkable series of researches contained in the whole field of Chemistry. Sabatier and Senderens (1897–1905) initiated, and Sabatier and Mailhe (1904–1908) and a number of other investigators extended, a principle that has since found enormous application both in the laboratory and industry, namely, that almost any compound capable of undergoing reduction, and almost all unsaturated organic substances, when vaporised, mixed with Hydrogen, and passed over a catalyst at a suitable temperature, are reduced or hydrogenated. The detailed researches were first described in the *Comptes rendus* of the French Academy of Sciences and in the *Bulletin de la Société Chimique de France* commencing in 1897. Collated accounts have been published in the *Annales de Chimie et de Physique*, 1905, (8), 4, 319, and 1909, (8), 16, 70 in *Berichte*, 1911, 44, 1984 and in Sabatier's book "La Catalyse en Chimie Organique," 1913.

Apparatus. A striking feature of Sabatier's work is the simplicity of the means employed. The apparatus consisted of (1) a Hydrogen generator, (2) a device for admitting the reacting substances, (3) the contact reaction tube, (4) apparatus for collecting the products.

Sabatier and Senderens made their Hydrogen by the action of fairly concentrated Hydrochloric acid on Zinc, and purified it by causing it to pass (a) a scrubber containing strong caustic Soda solution, (b) a scrubber containing strong Sulphuric acid, (c) a tube containing metallic Copper, heated to redness, to arrest compounds of Sulphur, Arsenic, etc., (d) a tower filled with granulated caustic Potash.

Hydrogen made from metals and acids requires elaborate purification, since small amounts of certain impurities especially compounds of Halogens, Sulphur, and Arsenic, which are liable to be present in gas made in this way, have a powerfully anticatalytic action on metal catalysts. Using electrolytic Hydrogen now commercially obtainable, such purification is less essential. Treatment with red hot Copper and granulated caustic Potash is nevertheless advisable, since only by complete freedom from certain impurities can satisfactory results be obtained.

Sabatier and Senderens' reaction tube was of glass 65–100 cm. long and 1.4 to 1.8 cm. internal diameter, with the catalyst disposed

along 35–80 cm. of its length. The tube was gas heated, and the temperature of the catalyst was recorded by a thermometer lying in as close proximity with it as possible. Other devices were employed when it was necessary to fix the temperature of the catalyst more accurately. A more convenient apparatus capable of simple and accurate temperature control is the following :—

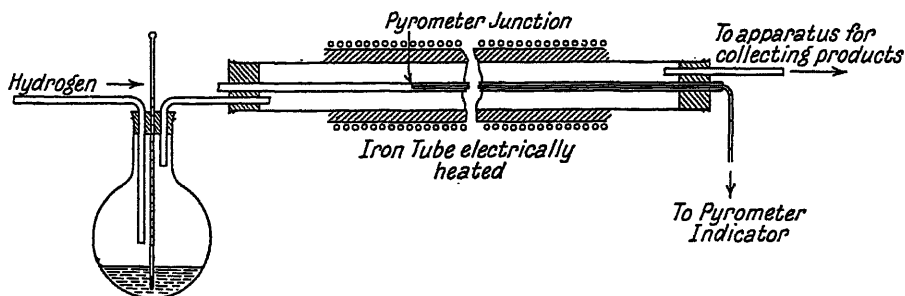


FIG. 11.

The reaction tube is of Silica about 100 cm. long and 3 cm. internal diameter. This is placed within an Iron tube wound with resistance wire for electrical heating. The temperature is recorded by means of a pyrometer, the insulated wires of which slide along a narrow glass tube running longitudinally through the silica tube. By moving the pyrometer junction along this

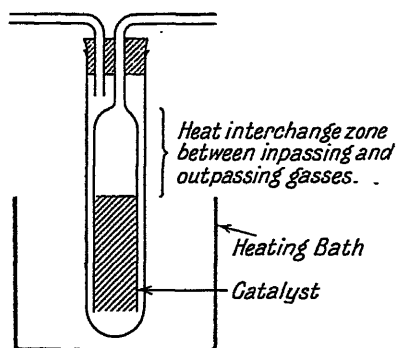


FIG. 12.

the pyrometer junction along this tube the temperature of the catalyst at any point can be measured and adjusted by altering the current passing through the electrical heating circuits. This can be done either by the use of a movable resistance or (more economically from point of view of current consumption) by altering the *E.M.F.*, using a variable transformer. If the Silica tube is of suitable length, the ends can be closed by rubber bungs, which carry inlet and outlet tubes of glass.

If the catalyst is in granular form, or mounted on a support such as pumice, the reaction tube can conveniently consist of a glass U-tube, heated in an air, oil, or metal bath, the temperature of which is indicated by a thermometer. Still better is a form of apparatus represented in Fig. 12, in which an equable catalyst temperature is maintained by heat interchange between the inpassing gases and the catalyst.

The manner of introducing the reactants depends upon their

physical properties. A gas can easily be mixed with the Hydrogen stream, both first passing through suitable flowmeters (for example, simple differential flowmeters) to indicate their rates and enable them to be adjusted. A liquid can be admitted by either of the following methods:—

(a) Sabatier and Senderens arranged a constant head of the liquid, and a constant gas pressure over it, and caused it to pass through a capillary to the reaction tube. The rate of entry of the liquid then depended on its viscosity and on the dimensions of the capillary tube.

(b) For liquids free from solid particles the adjoining sketch (Fig. 13) illustrates a simple arrangement. Adjustment of the tap enables a certain number of drops of liquid per minute to pass. The pressure-equalising tube ensures that variations of pressure on either side of the tap do not occur and affect the rate of drip. The Hydrogen supply can pass through the pressure-equalising tube.

(c) Using a vaporiser or carburetter. The Hydrogen is made to pass over, or through, the liquid, which is kept at a constant temperature in a vessel immersed in a suitable bath. Depending upon (1) the temperature of the bath, (2) the rate of passage of the Hydrogen, (3) the shape of the vessel, a certain definite proportion of the liquid is taken up as vapour by the passing Hydrogen. The concentration does not reach the saturation point unless the flow of gas is very slow, but a few trials suffice to show what temperature of the bath is necessary to produce a desired proportion. The tubes conveying the mixed Hydrogen and vapour to the reaction tube must be kept warm enough to prevent condensation of the latter.

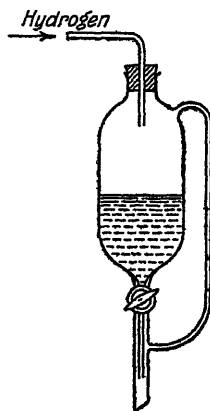


FIG. 13.

For low melting solids, Sabatier and Senderens employed method (a) above, maintaining the solid in a molten condition by immersing the whole in a heating bath. High melting solids were placed in a porcelain boat and inserted in the reaction tube. Either of the following simple arrangements seems preferable. Since the method of Sabatier and Senderens is only applicable to volatile substances, such a vaporiser as that described under (c) for liquids is equally practicable for solids. If the substance is very difficultly volatile, the vaporising chamber is best made in the form of a shallow closed pan, exposing a wide surface of molten substance. The Hydrogen, after passing over the melted surface, is conducted through wide, but short heated tubes, directly to the reaction tube.

The collection of products again depends upon their physical properties. Gases can be led directly to an absorbing liquid, gas-

holder or compressor. If liquid products are formed, a well-cooled coil condenser can be used, leading to a receiver closed except for an exhaust tube through which the gaseous products can pass to absorbing or collecting apparatus. High melting solids require for their reception a sublimation chamber, *e.g.*, a tin canister, fitted or cemented to the reaction tube, the passage being heated sufficiently to maintain the product in the vapour state until it emerges into the sublimation chamber.

Catalysts. The Sabatier and Senderens reaction employs finely-divided metal catalysts, *viz.*, Nickel, Cobalt, the Platinum metals, Iron, and Copper. The relative degrees of activity follow roughly the order mentioned. With the exception of the Platinum metals, they are prepared by precipitating the hydroxides or carbonates from a solution of an appropriate salt, thoroughly washing and drying the precipitate, and reducing with Hydrogen (free from catalytic poisons) in the chamber in which the catalyst is subsequently to be used. This procedure is desirable, since finely-divided Nickel, Cobalt, Iron, or Copper, when catalytically active, oxidise very easily in air, the first three being often pyrophoric. The pyrophoric properties of a finely-divided metal and its catalytic activity are not necessarily connected, but in the case of metals prepared by reduction in Hydrogen generally occur together, and may be regarded as probably depending on the same cause, *viz.*, power to occlude Hydrogen. Pyrophoric power is due to adsorbed Hydrogen, and disappears when all Hydrogen is displaced by an inert gas. In general, metallic catalysts are more active the lower the temperature at which they are reduced. When too high a temperature is employed in preparation, these metals are comparatively inert, and, unless heated, cease to be pyrophoric.

Nickel is much the most useful of the metals mentioned, being the only one capable in practice of effecting certain hydrogenations, such as that of the Benzene ring. Cobalt, Platinum, and Palladium, when freshly prepared, are capable of replacing Nickel in most reactions, but their activity is more variable, and often only temporary. For example, while Nickel will hydrogenate Benzene to Cyclohexane continuously for a month, Cobalt, Platinum, and Palladium are usually effective for a short time only. Iron can commonly replace Nickel, but not for hydrogenation of the Benzene nucleus, or reduction of oxides of Carbon to Methane.

Copper is by far the least active, but on this account possesses certain advantages. For instance it is the best catalyst for reducing aromatic nitro-compounds, since its action is completely restricted to the nitro-group, and a good yield of amine therefore results. It is less susceptible to poisons than Nickel, it is cheap, the oxide is easily reduced (Copper oxide is reduced by Hydrogen at 180° C.),

an unusually large choice of means is available for obtaining a deposit of catalytic Copper, and revivification of stale catalyst is simpler than in the case of either of the other metals.

The Platinum metals as catalysts stand in a distinct class. Platinum and Palladium generally behave similarly, though the latter is the more active. Commonly they are exceedingly energetic, Palladium, for example, being the most active catalyst known for hydrogenation of liquid oils. Gases are in many cases hydrogenated by Platinum or Palladium-black at the ordinary temperature, even Benzene, according to Lunge and Akunov, being slowly reduced (*Z. anorg. Chem.*, 1900, 24, 191). The activity of these metals is, however, always short-lived at a low temperature, and at higher temperatures they are often destructive. Platinum or Palladium-"black" are much more active than the spongy metals on account of the finer state of division.

The solubility of Hydrogen in metals at high temperatures, as determined by Sieverts and Krumhaar, follows closely their relative activities as hydrogenating catalysts (*Ber.*, 1910, 43, 893). Cadmium, Thallium, Zinc, Lead, Bismuth, Tin, Antimony, Silver, and Gold did not appreciably absorb

the gas, but the solubility curves of Hydrogen in Palladium, Copper, Nickel, and Iron are shown in the accompanying graphs (Fig. 14).

In the case of the last three metals, as the temperature rises up to the melting point, the solubility of Hydrogen steadily rises, and then, at the melting point, a sudden very considerable increase in solubility occurs. In the liquid metal, the solubility again steadily increases with rising temperature. With Palladium, however, the solubility is independent of the temperature up to the melting point, then abruptly diminishes to half, and again remains constant in the liquid metal.

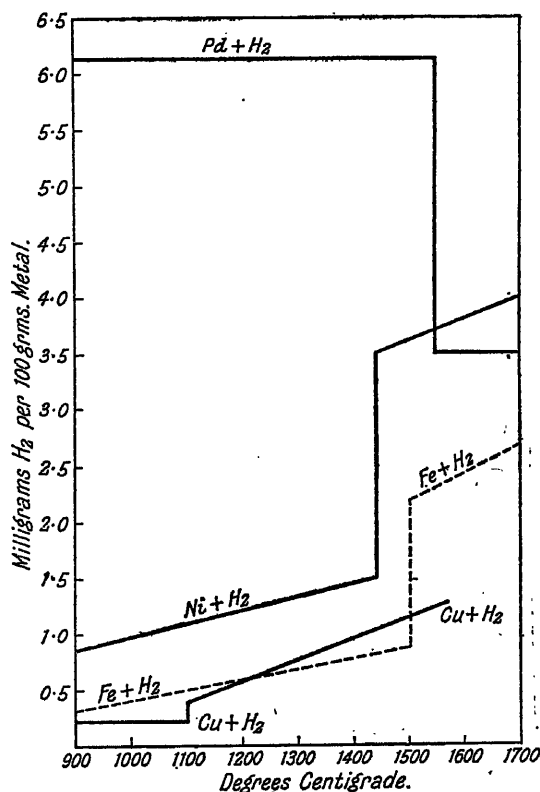


FIG. 14.

On cooling, the metals retain a small proportion of the dissolved Hydrogen. In the case of Iron, the evolution of gas at the solidification point is so violent that the tube containing it may be blown to pieces, leaving the metal in the form of a spongy regulus.

Very complete data, for varying pressures, are given in the papers mentioned, and by Sieverts in *Z. Phys. Chem.*, 1911, 591; 1914, 451.

Whichever metal is used, a state of fine sub-division is necessary so that the surface exposed may be a maximum. A support such as pumice, asbestos fibre, kieselguhr, Magnesium carbonate, etc. (free from anticatalysts) is sometimes an advantage. Sabatier, however, used catalysts in powder form without any support.

Preparation of Catalytic Nickel. Many modes of preparation of catalytic nickel have been described in the technical and patent literature. The best method depends somewhat on the particular purpose for which it is to be used, since the length of active life and susceptibility to poisons differ considerably according to the method of preparation.

Commercial Nickel is dissolved in pure Nitric acid, or a Nickel salt not containing any anticatalytic element is dissolved in water, and the oxide obtained from the solution as follows: 1. The solution is added to excess of caustic Soda or Sodium carbonate solution, and the precipitate thoroughly washed by decantation, finally using distilled water, then filtered, pressed, and dried. 2. The solution of nitrate is evaporated and the dry nitrate calcined to oxide at a dull red heat.

The first method was used by Sabatier, and gives the more active catalyst. If the oxide so obtained is reduced at 250° C., the metal obtained is exceedingly active, but very sensitive to poisons. By reducing at 280–300° C. a powerfully active catalyst is obtained, pyrophoric in air, which, in the absence of poisons, retains its activity for a long time. According to Sabatier, Nickel required for difficult hydrogenations, such as that of the Benzene ring, must be reduced from its oxide at a temperature below 300° C. This was confirmed by Darzens (*C.R.*, 1904, 137, 869) and by Brunel (*Ann. Chim. Phys.*, 1905, (8), 6, 205), who found that the higher the temperature of reduction the feebler was the activity of the resulting Nickel; hence hydrogenation of the Benzene ring is slow with catalysts prepared above 300° C., while reduction at a red heat yields a metal not pyrophoric, and catalytically inert. These conclusions require, however, some modification, since the time taken in reduction, and the presence of promoters, or a support, are important factors. Thus, a high temperature of reduction—even 600° C.—may be employed if the process is carried out in a sufficiently short time, while with certain siliceous supports, *e.g.*, kieselguhr, a higher tem-

perature than those mentioned by Sabatier is unavoidable. More recently, Sabatier himself has recognised the necessity of altering his original views, since Sabatier and Espil found that under certain circumstances Nickel could be reduced from its oxide above 350°C . and yet induce hydrogenation of the Benzene ring. Even when reduced at 500°C . and maintained at $500\text{--}700^{\circ}\text{C}$. in Hydrogen for 8 hours it was still active. After heating to 750°C ., however, it would no longer hydrogenate Benzene, although it still possessed the power of effecting reduction of nitro-bodies (*Bull. Soc. chim.*, 1914, 15, 779).

A deposit of catalytic Nickel on a support is obtained by soaking the latter in a solution of Nickel nitrate or formate or a suspension of the washed hydroxide or carbonate, drying, decomposing, and reducing in pure Hydrogen as before.

The presence of even minute traces of certain substances much reduces the catalytic activity of Nickel, and for some reactions—such as hydrogenation of the aromatic nucleus—completely suppresses it. Such poisons are compounds of Sulphur, Arsenic, Phosphorus, or halogens, more especially H_2S , AsH_3 , PH_3 , and halogen acids, and if they are present in either of the reagents their effect on the catalyst is cumulative. They are often present in Hydrogen made by interaction between metal and acid, or Iron and steam. Traces of Bromphenol in Phenol were found by Sabatier to prevent its hydrogenation to Cyclohexanol. On one occasion, pure Phenol in an open flask was exposed overnight to laboratory air which contained traces of Bromine fumes. On the following day it could not be hydrogenated. Sabatier also found that Benzene which contained a trace of Thiophene could not be hydrogenated owing to the poisonous effect of the Sulphur (Sabatier and Mailhe, *C.R.*, 1911, 153, 160).

In hydrogenation by Nickel, Sabatier and Senderens distinguished three stages: (1) A short latent period during which the catalytic surface is adapting itself to its function. This is of short duration, and due to the superficial changes that the catalyst must undergo when first subjected to the reacting substances before it can exert its characteristic action. (2) A period of normal activity. This is generally very long and would perhaps be indefinite if it were possible to prevent the introduction or formation of deleterious substances. With pure Hydrogen and pure volatile substances, the same specimen of Nickel should be active for several months. Eventually, however, the activity of the catalyst begins to decline, the more active the metal originally the sooner the change. Traces of anticatalysts accumulate, including small quantities of non-volatile matter derived from the substance undergoing reduction. When Nickel which has become enfeebled is dissolved in Nitric acid, a foetid

smell of hydrocarbons is always produced, and a brown, tarry residue remains. Deposition of material on the catalyst quickly destroys its activity, and may arise in several ways besides decomposition, such as when the reaction produces substances only slightly volatile. Sabatier instances the hydrogenation of Aniline in which two of the products Dicyclohexylamine and Cyclohexylaniline have very low vapour pressures at the reaction temperature. A sudden lowering of the temperature of the catalyst may also cause deposition, and raising the temperature and vaporising the deposit does not always restore the catalyst's activity. (3) Period of decline. A catalyst which has lost its activity can be restored, but only in an inferior degree, by oxidising the metal and its accumulated impurities and reducing at a low temperature. The presence in the catalyst of suboxides of Nickel or of combined water appears to be necessary for high catalytic activity.

Preparation of Cobalt. Catalytic Cobalt, like Nickel, is made by reduction of the finely-divided oxide with pure Hydrogen. A temperature of at least 350° C. is, however, necessary, which perhaps accounts for the inferior catalytic powers of Cobalt. Cobalt has no advantage over Nickel, and many disadvantages. It is more difficult to prepare, less active, and therefore requires a higher temperature in use, with correspondingly increased risk of side reactions or decomposition. Also it more quickly becomes enfeebled and inert.

The Platinum Metals. These metals are used more as oxidising catalysts and in the hydrogenation of liquids. For gas phase reductions they are seldom useful, since, though they may be powerfully active at first, this activity does not last.

A finely-divided form of Platinum, "Platinum sponge," was first prepared by E. Davy by gently heating the sparingly soluble double chloride of Platinum and Ammonium. The product was a porous mass, which became denser on heating, and assumed a lustrous metallic surface on burnishing. Palladium sponge is made in the same way.

A more finely-divided form of Platinum or Palladium is obtained when a solution of a Platinum or Palladium salt is treated with a reducing agent, which causes the metal to separate as a dark powder, known as Platinum or Palladium "black." Various reducing agents have been employed, namely, alcoholic caustic Soda or Potash (Zeisse, *Pogg. Ann.*, 1827, 9, 632; Liebig, *ibid.*, 1829, 17, 102); Sodium formate (Dobereiner, *ibid.*, 1833, 28, 181), Sodium tartrate (Cooper, *Quart. J. of Science*, Vol. 5, 120); Metals in acid solution, especially Zinc and Magnesium (Bottger, *J. pr. Chem.*, 1870, (2), 2, 137); an alkaline solution of Glucose or Glycerol (Zdrawkowitch, *Bull. Soc. chim.*, 1876, (2), 25, 198), and Formaldehyde (Loew, *Ber.*, 1890, 23, 289). The method of Loew is the most convenient, and

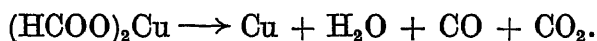
consists in dissolving Platinic chloride (50 grams) in water (50–60 c.c.), adding Formaldehyde (70 c.c. of 40 per cent. solution), well cooling, and then running in, drop by drop, a solution of caustic Soda (50 grams) in an equal weight of water. After standing for 12 hours, the finely-divided metal is collected in a filter and washed with water until a deep black liquid begins to pass through. Washing is then stopped, until, after a time, the metal has become a loose and porous mass, when washing is continued until all traces of chlorides—which exert a deleterious action—have been dissolved away. The metal is then quickly pressed, and dried in a desiccator over strong Sulphuric acid.

Preparation of Iron. For some catalytic purposes, pure Iron is not essential, and fine powder or even wire may be used. For hydrogenation, however, even the purest commercial form is unsuitable and reduction of the oxide is necessary. The oxide may be made as follows: 1. By precipitation from a solution of a ferric salt with caustic Soda, Ammonia, or Sodium or Ammonium carbonate. The precipitate is thoroughly washed, filtered, pressed, and dried. 2. By heating Iron nitrate or basic acetate alone or in a current of steam. 3. By burning commercial Iron wire in Oxygen. The magnetic oxide so formed is free from poisonous impurities present in the original metal. When prepared by either of methods 1 or 2, the Iron oxide can be mounted on a support. Reduction of the oxide is then carried out in the catalytic reaction chamber, using pure Hydrogen and the lowest possible temperature. The reduction is very slow below 400°C ., and even at $400\text{--}450^{\circ}\text{C}$. requires six or seven hours to complete. The narrow temperature range for reduction is the chief disadvantage to the use of Iron, since at temperatures above 480°C . the resulting metal is not pyrophoric and its catalytic activity is weak.

Iron can be used for reducing unsaturated organic substances, aldehydes, and ketones. It will not hydrogenate the Benzene ring, or, except at increased pressure, reduce oxides of Carbon to Methane.

Preparation of Copper. Copper may often be employed in the form of commercial Copper powder. It may also be prepared by either of the following methods: 1. Precipitation from a solution of a Copper salt by addition of Zinc dust. The fine Copper is washed with air-free water containing very dilute acid to dissolve Zinc oxide, then with distilled water, and stored as a paste. Drying (which can be facilitated by a final washing with an easily volatile solvent) must be completed in an inert atmosphere, preferably in the reaction chamber in which the material is to be used. 2. Oxide or carbonate is precipitated from a solution of a Copper salt by addition of caustic Soda or Sodium carbonate, and washed, filtered, pressed, and dried. Alternatively, the oxide is obtained by ignition of metallic Copper in

air, or of a suitable salt, such as the nitrate. The oxide is then slowly reduced, preferably below 200° C. in a current of pure Hydrogen. Prepared at a low temperature, Copper possesses its maximum catalytic activity, and if poisons are excluded always behaves in the same way. Rapid reduction of Copper oxide leads to overheating, often to incandescence, due to the heat generated in the reaction, and therefore yields an inferior catalyst. Irregularities in action, which are common with Copper, are chiefly due to differences in the temperature of reduction. 3. An active deposit of Copper on a support can be made by soaking the latter in a solution of Copper formate, drying and decomposing in an inert atmosphere,



On account of its moderate activity, Copper is the most useful of the reducing catalysts for certain reactions, for example, reduction of nitro-compounds to amines, which takes place without side reactions. Its action is sometimes different from that of the other metals, since, at the high temperature it requires, the reverse reaction, dehydrogenation, may be the predominating one. Thus while Nickel, Iron, and the Platinum metals reduce aldehydes and ketones to alcohols, Copper effects the reverse change, and dehydrogenates alcohols to aldehydes or ketones.

General Principles of Sabatier and Senderens' Reaction. The method of Sabatier and Senderens constitutes one of the most general, and at the same time most powerful, methods of reduction known. The stability and volatility of the initial and final substances impose the chief limitations, and these have been completely overcome by the later developments arising from the researches of Ipatiev, Paal, Skita, and Willstätter, who employ liquid media and Hydrogen under pressure. As a consequence, the catalytic method can be applied to hydrogenation of almost any substance except those containing a catalytic poison.

The range of temperature over which a reaction will take place is sometimes wide, for example, reduction of ethylenic compounds or oxides of Carbon with Nickel, or reduction of nitro-compounds with Copper. These reactions are easy to carry out and give good yields. In other cases, the range is narrow, as in hydrogenation of the aromatic nucleus, where temperatures approaching 200° C. are necessary for a practicable rate of reaction, while above 200° C. bye-reactions supervene.

Finely-divided metal catalysts exert a hydrogenating action at temperatures below a certain point, this point depending upon the particular substance and metal employed. Above this temperature the reverse change, dehydrogenation takes place, even in presence of excess of Hydrogen. At the same time, under the influence of a

high temperature and an active catalyst, more or less degradation ("cracking") of the molecule occurs, together with hydrogenation of the degradation products, and sometimes a recombination between them, as in the synthesis of petroleum-like bodies from such simple hydrocarbons as Acetylene and Ethylene. It is therefore impossible to study the catalytic action of metals upon mixtures of Hydrocarbons and Hydrogen, as though a simple reversible reaction were involved,

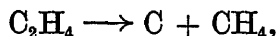


in which the equilibrium depended upon the temperature, since the reactions are rarely simple, especially at temperatures above 200°C .

In the year preceding that in which Sabatier and Senderens commenced their researches Moissan and Moureau (*C.R.*, 1896, 122, 1240) observed that Acetylene reacted vigorously when passed at the ordinary temperature over Platinum sponge, finely-divided Iron, Cobalt, or Nickel which had been reduced from their oxides at a low temperature. Metals prepared at a red heat required heating to cause this reaction. Much heat was generated, and with a swift gas current the metals became incandescent. The products of the action were chiefly Carbon and Hydrogen, but some of the Acetylene was polymerised to Benzene. Moissan and Moureau suggested that the energetic absorption of the gas by the porous metal developed sufficient heat partly to decompose and partly to polymerise the Acetylene. Once the decomposition had commenced the internal energy of the Acetylene augmented the reaction.

Action of Catalytic Metals on Ethylene. Pure Ethylene is not attacked by Nickel below about 300°C . Above this point, the metal gradually intumesces, giving finally a black, bulky mixture of Carbon and Nickel (Sabatier and Senderens, *C.R.*, 1897, 124, 616, 1358). The metal is most vigorous when prepared at a low temperature, but it is still active for this reaction when made at a red heat, while even Nickel filings, though irregular, cause reaction at a higher temperature ("cracking"). The products of reaction are Ethane, Methane, and Hydrogen, with traces of higher paraffins.

In their first paper, Sabatier and Senderens formulated the main reaction,



and did not understand the origin of the Hydrogen. In their later paper, they recognised the formation of Ethane and correctly expressed the main reaction as follows :



The Ethane then decomposed into Methane and Carbon, while the former gradually decomposed further into Carbon and Hydrogen.

Direct experiment confirmed these views, since Ethane in contact with Nickel at 350° C. partially decomposed in this way, and at a still higher temperature, about 390° C., Methane gave Carbon and Hydrogen. A long column of Nickel exerted the same action at a high temperature, and even at 325° C. Ethylene could be completely degraded into Methane, Carbon, and Hydrogen.

Platinum and Copper had no action on Ethylene below 400° C., but Cobalt induced reaction about 360° C. Iron above 350° C. caused reaction, but less vigorously than Nickel or Cobalt. The products consisted of Ethane, Methane, and Hydrogen, as before, together with Carbon, which remained with the catalyst (*C.R.*, 1900, 181, 267).

Action of Catalytic Metals on Acetylene. When Acetylene is passed over finely-divided reduced Copper at 180–250° C., there is first a vigorous absorption of the gas, soon followed by formation of solid, liquid, and gaseous products. The gaseous products are Hydrogen, unchanged Acetylene, olefines (Ethylene, Propylene, etc.), and Ethane. The liquid, which can be separated by a well-cooled condenser, consists of a mixture of olefinic and aromatic hydrocarbons, while the solid product which remains with the Copper is a hydrocarbon, "Cuprene," so designated on account of its mode of formation (*Bull. Soc. chim.*, 1899, 21, 530; *C.R.*, 1900, 130, 250). The formation of Cuprene causes the Copper to swell, so that it repeatedly blocks the tube. By prolonged treatment with Acetylene, the Copper becomes replaced by a yellow mass of Cuprene and Copper, containing about 1.8 per cent. of the latter. Catalytic action then ceases. Close examination shows the mass to consist of microscopic filaments which compress into a substance resembling tinder.

Cuprene is a non-volatile hydrocarbon the composition of which corresponds with the formula $(C_7H_6)_n$, and it is doubtless identical with the substance obtained by Erdmann and Köthner (*Z. anorg. Chem.*, 1898, 19, 48) and by Alexander (*Ber.*, 1899, 32, 2381). Erdmann and Köthner passed Acetylene over hot spongy Copper, and noticed that at 400–500° C. complete decomposition to Carbon and Hydrogen occurred, while at 250° C. "the Copper combined with the gas to give a voluminous yellowish-brown mass which is not explosive." They nevertheless regarded the substance as a compound of the nature of an acetylide, and gave it the formula $C_{44}H_{64}Cu_3$. Alexander found that at 250° C. Acetylene caused Copper to swell enormously, giving a uniform mass, and that the action continued until the product contained 2 per cent. only of Copper. The formation of liquid products was also noticed, and the solid mass, after separation of these, was found to be odourless, and to give up its Copper in boiling with dilute acid. Alexander correctly concluded that Copper was retained in Cuprene mechanically, and that the

reaction consisted in polymerisation of the Acetylene, with formation of Naphthene-like hydrocarbons.

Sabatier and Senderens found that Cuprene is insoluble in all ordinary solvents, that it is not attacked by strong Sulphuric acid, but gives nitro-compounds with Nitric acid. Above 400°C ., it decomposes into a mixture of volatile hydrocarbons and leaves a residue of Carbon.

The formation and properties of Cuprene were further investigated by Kaufmann and Schneider (*Ber.*, 1922, 55 B, 267), and by Kaufmann and Mohnhaupt (*Ber.*, 1923, 56 B, 2533). The residue obtained by heating Copper ferrocyanide in air to 250°C . for 15 minutes was found to be a much more efficient catalyst for Cuprene formation (at $220\text{--}340^{\circ}\text{C}$.) than pure Copper or either of its oxides. Working with pure Acetylene, they found that when Oxygen was completely absent both from the catalyst and the gas, no Cuprene was found. It was supposed in consequence that the first stage of the reaction consisted in the formation of a complex compound or Acetylide between the Acetylene and an oxide of Copper, which then decomposed pyrogenously (compare, however, Willstätter's observations on the rôle of Oxygen). Oil in small quantities was always formed simultaneously with Cuprene; which was further shown not to be a homogeneous substance, but to vary in composition between $(\text{C}_{11}\text{H}_{10})_n$ and $(\text{C}_{15}\text{H}_{10})_n$, according to the details of preparation. Dilute Nitric acid oxidised it to Mellitic acid.

When Nickel, reduced at 300°C ., is used instead of Copper, and a fast current of Acetylene passed, the metal quickly becomes incandescent. This is due to occluded Hydrogen, since after displacement by Nitrogen no appreciable action on Acetylene is induced by Nickel until a temperature of 180°C . is reached (Sabatier and Senderens, *C.R.*, 1900, 131, 187). At 180°C . or above, reaction takes place without incandescence so long as the Acetylene stream is not too fast, and solid liquid and gaseous products are formed. The solid products are Carbon and Cuprene, which remain on the catalyst. A well-cooled condenser separates a light oil, which is a mixture of aromatic and higher olefinic hydrocarbons. It will be necessary to study the formation and properties of this liquid in greater detail later. The gaseous products consist of a mixture of Hydrogen, Ethane, Ethylene, and unchanged Acetylene.

Using a rapid stream of Acetylene, the Nickel becomes incandescent, and the well-known polymerisation reaction of Acetylene to Benzene is superposed on the catalytic reactions. The issuing gas then consists of 50 per cent. of Hydrogen, 36 per cent. of Ethane, 2 per cent. of Ethylene, with 10 to 12 per cent. of condensible hydrocarbons, largely Benzene and homologues.

Platinum has no action on pure Acetylene until a temperature

of about 150° C. is reached, when reaction commences with intumescence. The products are Carbon, Ethylene, Ethane, a little Hydrogen, and small quantities of Benzene.

With Cobalt, Acetylene commences to react about 200° C., and decomposes almost completely as with Nickel. Iron behaves similarly, but less Ethane is formed, and in addition to Carbon and Hydrogen the chief products are olefines and Benzene (*C.R.*, 1900, 131, 267).

Hydrogenation of Ethylene. When Ethylene is passed with Hydrogen over catalytic Nickel at temperatures above 30° C., Ethane is formed. The reaction is strongly exothermic. At 130–150° C., the action is rapid and smooth, and a gas mixture of suitable composition yields nearly pure Ethane (Sabatier and Senderens, *C.R.*, 1897, 124, 1359; 1900, 130, 1761; 131, 140). Using excess of Hydrogen, all the Ethylene is reduced to Ethane, while if excess of Ethylene is present the Hydrogen is all used, and a mixture of Ethane and Ethylene results. From such a mixture, the Ethylene can be absorbed by Bromine, and pure Ethane obtained. At higher temperatures, Nickel acts destructively. At 300° C., a deposit of Carbon is formed on the catalyst, and Methane is produced, together with a small proportion of more complicated hydrocarbons, some of which are liquids.

Cobalt and Iron similarly effect reduction of Ethylene to Ethane, but less vigorously than Nickel. For a time Cobalt acts at the ordinary temperature, but its action quickly stops as it becomes carbonised. It must then be heated to 100–150° C., when its action is more permanent.

Copper directly hydrogenates Ethylene to Ethane in good yield at temperatures between 180° and 300° C. Secondary reactions are almost absent, and there is no deposit of Carbon. Freshly-made Platinum-black, as first shown by de Wilde (*Ber.*, 1874, 7, 352), causes Ethylene and Hydrogen to combine at the ordinary temperature, with generation of heat. This action is only transient, since carbonisation of the Platinum soon suppresses its activity. Action recommences on heating the Platinum, but it is not permanent until 180° C. is reached, when conversion into Ethane is almost quantitative. Spongy Platinum is inert at the ordinary temperature, but behaves like Platinum-black at 180° C.

The technical production of Ethane—selected on account of its low boiling point (–93° C.) as the working substance in a refrigerating machine—has been described by Sprent (*J. Soc. Chem. Ind.*, 1913, 32, 171). Ethylene made by dehydration of alcohol must be purified from Ether, and small quantities of dehydrogenation products, viz. Acetaldehyde, Isoprene, etc., to avoid poisoning catalytic Nickel and contaminating the Ethane. Removal of these substances was

accomplished by condensation at 50 atmospheres pressure, but the Ethylene still was not sufficiently free from anticatalysts. Traces of Sulphuretted hydrogen (derived from sulphates in the Alumina used for preparing the Ethylene) were removed by washing with Lead acetate solution, and further unidentified impurities by scrubbing with Sulphuric acid.

Hydrogen and Ethylene purified in this way were mixed in equal volumes with the aid of suitable flowmeters, and passed to the Nickel catalyst mounted on pumice, contained in four iron tubes, each 1 metre long and 8 cm. internal diameter. The gas first passed through two of the tubes "in parallel," then mixed and passed the remaining two tubes similarly arranged. The dimensions of the tubes, and their arrangement, were so chosen that at a convenient gas velocity (2 cubic metres per hour) the heat of reaction was approximately balanced by the heat radiated, so that the temperature could never rise to the point at which Ethane decomposed, and the reaction temperature of 200° C. was maintained with but small application of external heat.

Under such conditions, however, the highest conversion that could be obtained per passage was only 10 per cent. Chemical methods of extracting this small percentage were unavailing; and although the Lindé liquefaction method gave promising results, it was deemed more expedient to effect the combination of Ethylene and Hydrogen under pressure, and obtain complete combination to Ethane. Under these circumstances, however, at 30–40 atmospheres, the heat generated in the reaction introduced new complications, conveniently overcome by diluting the interacting gases with Ethane, using a mixture of 80 per cent. Ethane and 10 per cent. each of Ethylene and Hydrogen. When this mixture was passed through an Iron reaction chamber filled with Nickelised pumice, maintained at 200° C., pure Ethane emerged, which could be immediately condensed.

This plant, situated at Bitterfeld, manufactured 25 kilos. of liquid Ethane per day.

Hydrogenation of Acetylene. When a mixture of Hydrogen and Acetylene is passed over Nickel at the ordinary temperature, action occurs with generation of heat (Sabatier and Senderens, *C.R.*, 1899, 128, 1173). The composition of the product depends on the relative proportions of Acetylene and Hydrogen, the temperature of the catalyst, and the speed of the gas current. With sufficient Hydrogen, Ethane is the main product, but Ethylene is also formed and liquid products, mainly paraffins, with some olefines and a small quantity of Benzene. A small amount of Carbon is deposited on the Nickel, which otherwise remains unchanged. The proportion of liquid products is greater the higher the temperature and the lower the proportion of Hydrogen in the reacting gases. Eventually, with a low proportion of Hydrogen, the nickel intumesces and becomes

incandescent, as observed by Moissan and Moureau, and a considerable proportion of aromatic and hydroaromatic hydrocarbons is then produced.

When Acetylene with excess of Hydrogen is passed over Iron, there is no action at the ordinary temperature, but above 180°C . action commences, with formation of Ethane, Ethylene, and higher hydrocarbons of these series, together with small quantities of Benzene and homologues. The condensible product boils between 50°C . and 250°C ., and is said to resemble the natural petroleum of Canada (Sabatier and Senderens, *C.R.*, 1900, 130, 1628).

With excess of Hydrogen, Cobalt above 180°C . converts Acetylene fairly completely into Ethane. Some liquid products are formed, however, the proportion of these increasing as the temperature is raised.

Freshly-prepared Platinum-black converts a mixture of Acetylene and excess of Hydrogen into Ethane rapidly at the ordinary temperature. Small quantities only of other products are formed, but the catalyst soon becomes inert. At 180°C ., hydrogenation is rapid and continuous, accompanied by more complicated changes, giving rise to liquid hydrocarbons, as in the case of the other metals. Raising the proportion of Acetylene increases the formation of Ethylene and liquid hydrocarbons, but some Ethane is always produced. Still higher proportions of Acetylene lead to incandescence and carbonisation of the catalyst with a greater proportion of Acetylene polymerising to Benzene. Spongy Platinum has no action at the ordinary temperature, but at 180°C . behaves like Platinum-black (*C.R.*, 1900, 131, 40).

When a mixture of Acetylene and an excess of Hydrogen is passed over actively catalytic Copper, action commences at 130°C . More compact Copper requires a higher temperature. Ethane is formed and a certain proportion of liquid hydrocarbons. As the proportion of Acetylene is increased, Cuprene commences to form and the gaseous product contains Ethylene. With a mixture very rich in Acetylene, quantities of liquid hydrocarbons, olefinic and aromatic, containing Benzene, homologues, and Styrene, are formed (*C.R.*, 1900, 130, 1559).

Much attention has been given to the problem of the technical preparation of Ethylene by hydrogenation of Acetylene, and considerable success has been claimed by using as catalyst a metal of the Platinum group diluted with a base metal (Karo, D.R.-P. 253160). When a Nickel catalyst is used, Ethane is always produced in large quantity, and the formation of more complex bodies of the nature of petroleum cannot be altogether prevented.

The difficulty of obtaining a high yield of Ethylene when Acetylene and Hydrogen in equal volumes are brought into contact with Nickel

is due to the very powerful affinity with which the metal absorbs the gases, especially Hydrogen. Thus, Ross, Culbertson, and Parsons have shown that the absorbing capacity for Hydrogen of a highly active catalytic Nickel exceeds that of any form of charcoal, and that, in consequence, at the reacting surface excess of this gas always tends to be present, with the result that Ethane is formed to a greater or lesser degree. By repeatedly admitting fresh quantities of an equimolecular mixture of Acetylene and Hydrogen to freshly-reduced catalytic Nickel, these investigators found that as soon as the adsorbed Hydrogen had been consumed an 80 per cent. yield of Ethylene could be obtained (*J. Ind. Eng. Chem.*, 1921, 775).

Sabatier and Senderens' Theory of Formation of Natural Petroleum. The experiments just described show that Acetylene reacting in contact with finely-divided metals carbonises with intumescence and incandescence of the catalyst, as observed by Moissan and Moureau, and formation of a small quantity of liquid hydrocarbons. The mechanism of this reaction is probably as follows: Acetylene is a reactive and an unstable substance, easily attacked at the treble linkage between the Carbon atoms. At a high temperature, and especially in contact with a suitable catalyst, rupture of the treble linkage occurs, setting free "nascent" :CH groups. In the presence of Hydrogen and a hydrogenating catalyst, :CH groups are hydrogenated to :CH_2 , $\cdot\text{CH}_3$, and CH_4 . The residues :CH , :CH_2 and $\cdot\text{CH}_3$ are then able to reunite in a multiplicity of ways to form hydrocarbons of greater or lesser complexity and of almost any structure, or to break up completely into Carbon and Hydrogen. Hence when Acetylene, with or without Hydrogen, is subjected to the action of a catalytic metal, Carbon, Hydrogen, and hydrocarbons of all degrees of complexity are obtained.

By passing Acetylene and excess of Hydrogen over Nickel at 200°C . for 28 hours, Sabatier and Senderens collected about 20 c.c. of a clear yellow liquid of a beautiful fluorescence and an odour like that of petroleum. It commenced to boil at 45°C ., and half distilled below 150°C . At 250°C ., the residue was a yellowish-orange liquid, very fluorescent, containing polycyclic hydrocarbons. The specific gravity of the distillate was 0.791 at 0°C . It was only slightly affected by a mixture of strong Sulphuric and Nitric acids, showing that unsaturated and aromatic hydrocarbons were present in small quantities only. The specific gravity of the residue stable to the acid mixture was 0.753 at 0°C ., and it consisted of paraffin hydrocarbons (Pentane, Hexane, etc.). In density, odour, fluorescence, and composition (low content of unsaturated and aromatic bodies), the liquid closely resembled Pennsylvanian petroleum.

When pure Acetylene without Hydrogen was passed over heated Nickel, the Nickel became strongly incandescent, and the Acetylene

mainly decomposed into Carbon and Hydrogen. Part, however, polymerised to Benzene, Styrene, and other aromatic hydrocarbons, which, in a part of the Nickel column at a hydrogenating temperature ($200\text{--}250^{\circ}\text{C.}$), were partially hydrogenated to the corresponding Cyclohexane derivatives. Yet another portion of the Acetylene split into :CH residues which hydrogenated and reunited to form paraffin and olefine hydrocarbons. Using pure Acetylene, therefore, a liquid rich in aromatic hydrocarbons, and containing Cyclohexane, paraffin, and olefine hydrocarbons, was obtained. This mixture was fluorescent, green by reflected light and red by transmitted, and resembled crude Galician or Rumanian petroleum. By submitting it to further hydrogenation with Nickel at 200°C. , a colourless liquid was obtained hardly attacked by Nitric or Sulphuric acids, and composed of hydroaromatic and paraffin hydrocarbons. In composition it therefore resembled Caucasian petroleum, and on fractionation it gave a series of distillates corresponding in physical properties with those obtained similarly from the natural sources.

Mixtures of Acetylene and Hydrogen of varying composition, and conditions of reaction which altered the relative proportion of Acetylene undergoing polymerisation or paraffin formation, respectively, enabled petroleum of almost any intermediate composition between those of Pennsylvania and the Caucasus to be obtained. Hence, the wide variation in the composition of different petroleum could be easily accounted for by (1) differences in the proportions of Acetylene and Hydrogen interacting, (2) varying conditions of reaction, (3) different sequence of the reactions involved—polymerisation, degradation, and hydrogenation.

Cobalt, and to a certain extent Iron and other metals, are able to effect similar reactions. Sabatier and Senderens therefore accounted for the formation of natural petroleum as follows: The conditions under which the earth's crust originally formed were consistent with the production of large masses of the alkali and alkaline-earth metals and their carbides. Subsequent formation of water generated Hydrogen and Acetylene from these substances in widely varying proportions. When the Hydrogen was in great excess, subsequent catalytic action of a metal impregnated in adjacent rocks produced American petroleum and natural gas, such as exists around Pittsburg, consisting of Methane, Ethane, and Hydrogen. When Acetylene containing little or no Hydrogen was brought into contact with a hot metal, aromatic hydrocarbons were formed, which by the subsequent action of Hydrogen in contact with the same metal were transformed into Caucasian petroleum.

Intermediate conditions, such as the association of Acetylene with varying proportions of Hydrogen, produced intermediate mixtures, and conditions which produced mixtures of aromatic and paraffin

hydrocarbons without providing for the subsequent hydrogenation of the former produced the petroleum of Galicia and Rumania. The presence of Ammonia or of optically active bodies in natural petroleum does not invalidate this theory, since the former could readily be obtained from metallic nitrides, while dissolution of matter originally of biological origin would explain the presence of the latter (Sabatier and Senderens, *C.R.*, 1899, 128, 1173; 1900, 131, 187; 267, 1902, 134, 1185).

Hydrogenation of Ethylenic Compounds

Ethylenic linkages are easily hydrogenated in presence of catalytic metals. When another reducible group is present in the same molecule, it is generally possible by adjustment of conditions to hydrogenate the ethylenic linkage only. In most cases Nickel, Cobalt, Iron, Platinum, Palladium, or Copper can be used.

Hydrocarbons. Hydrocarbons of the Ethylene series up to C_8 have been reduced to the corresponding members of the paraffin series by the action of Hydrogen and finely-divided Nickel (*C.R.*, 1902, 134, 1127).

With Ethylene, action commences at $30^\circ C$. Other simple members of the series (*e.g.*, Propylene) react slowly at the ordinary temperature. Hydrogenation is faster as the temperature is raised, and up to $165^\circ C$. paraffin hydrocarbons are obtained quantitatively and pure. Above $200^\circ C$., partial disruption of the hydrocarbon chain occurs and paraffins of lower molecular weight are obtained. At $300^\circ C$., degradation is very fast, and small proportions of complicated hydrocarbons are also formed. Propylene, $CH_3 \cdot CH : CH_2$, with excess of Hydrogen, in contact with catalytic Nickel, at temperatures between 20° and $200^\circ C$., gives Propane only. When the Propylene is in excess, especially above $200^\circ C$., liquid hydrocarbons with the odour of petroleum are also formed, together with much Methane, Ethane, and Carbon.

By using weakly catalytic Nickel, unable to hydrogenate the Benzene ring, it is possible to hydrogenate unsaturated linkages without attacking the ring. Thus, Styrene, $C_6H_5 \cdot CH : CH_2$, may be made to give either Ethyl benzene or Ethyl cyclohexane quantitatively, according to the catalytic activity of the Nickel. With weakly active Nickel, Sabatier and Murat (*C.R.*, 1913, 156, 184) hydrogenated the three Cresyl propenes quantitatively to the ortho-, meta-, and para-Cymenes.

Cobalt and Iron can be used in these reactions instead of Nickel, but require a higher temperature. Platinum can also be used, and for a time will hydrogenate either Ethylene or Propylene at the ordinary temperature, but its activity is not long maintained. Reduced Copper above $180^\circ C$. can also be used in most cases. The

only exceptions can be stated generally. (1) If one of the CH_2 : groups composing the ethylenic linkage is substituted, then Copper will not effect hydrogenation. For example, Trimethyl ethylene, $(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CH}_3$, β -Hexene, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot\text{CH}_3$, and Stilbene, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_5$, are not reduced by Copper (Sabatier and Senderens, *C.R.*, 1902, 134, 1127). (2) Copper will not hydrogenate a partially reduced Benzene ring, *e.g.*, Cyclohexene, or Methyl cyclohexene (Sabatier and Senderens, *C.R.*, 1901, 132, 1256).

Copper, which is much less energetic than the other catalytic metals, often enables a reaction to be carried out without any complications when a more active catalyst would lead to further action. Thus, Styrene, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}_2$, gives Ethyl benzene easily with Copper, but yields more or less Ethyl cyclohexane with Nickel (Sabatier and Senderens, *C.R.*, 1901, 132, 1255). Limonene, $\text{CH}_3\cdot\text{C}_6\text{H}_8\cdot\text{C}\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_3 \end{smallmatrix}$, which gives Menthane with Nickel with Copper at $180\text{--}200^\circ\text{C}$. (which does not attack the Cyclohexene ring), gives only Dihydrolimonene, isomeric with Menthene (Sabatier and Senderens, *C.R.*, 1901, 132, 1256). With a Copper catalyst, water gas can be used to hydrogenate ethylenic compounds (Sabatier, F.P. 394957 of 1907).

Ethylenic Alcohols can be hydrogenated without affecting the hydroxyl group.

Allyl alcohol, $\text{CH}_2:\text{CH}\cdot\text{CH}_2\cdot\text{OH}$, hydrogenated with Nickel at $130\text{--}170^\circ\text{C}$., gives Propyl alcohol, with traces of Propyl aldehyde (Sabatier, *C.R.*, 1907, 144, 879). The same reaction is effected by the other metals, including Copper, at 180°C .

Unsaturated Acids of the Ethylenic Series are easily hydrogenated to the corresponding fatty acids.

Crotonic acid, $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{COOH}$, with Nickel at 190°C ., gives Propionic acid, and Oleic or its isomer, Elaidic acid, with Nickel at $280\text{--}300^\circ\text{C}$., are hydrogenated nearly quantitatively to Stearic acid. (Sabatier and Mailhe, *Ann. Chim. Phys.*, 1909, (8), 16, 70.) The other metals effect the same reactions.

Darzens (*C.R.*, 1907, 144, 328), working with esters of unsaturated acids, pointed out that the catalytic method of reduction differed in important respects from the other common chemical methods. Among the most powerful of the latter is the method of Bouveault and Blanc, who dissolve the substance to be reduced in boiling Alcohol, and add metallic Sodium (*C.R.*, 1903, 136, 1676, and many subsequent papers). Sodium and boiling Alcohol reduce the $\cdot\text{COONa}$ group to $\cdot\text{CH}_2\cdot\text{OH}$, and hydrogenate the Benzene ring and ethylenic groupings which are in an $\alpha\beta$ -position with respect to a $\cdot\text{COOH}$ group. Catalytic hydrogenation, on the other hand, leaves intact the $\cdot\text{COOH}$ group, hydrogenates the aromatic nucleus or not, according to the catalyst

used and conditions of the experiment, and reduces an ethylenic grouping whatever its position.

Esters of Unsaturated Acids are easily reduced to the esters of the saturated acid, whatever the position of the double linkage. Darzens (*C.R.*, 1907, 144, 328; *Bull. Soc. chim.*, 1907, (1), 4, 179) describes many hydrogenations of unsaturated esters; for example, Ethyl acrylate and Hydrogen, in presence of catalytic Nickel at 180° C., give quantitatively Ethyl propionate. Phenyl isocrotonic ester, $C_6H_5 \cdot CH:CH \cdot CH_2 \cdot COOC_2H_5$, likewise gives Phenyl butyric ester.

By condensing ketones of the type $R \cdot CO \cdot CH_3$ with Chloroacetic ester by the method of Reformatzky, and dehydrating the product with Phosphoric anhydride, Darzens obtained unsaturated esters of the type $\begin{matrix} R \\ \diagup \\ CH_3 \end{matrix} C:CH \cdot COOC_2H_5$, which on catalytic hydrogenation gave the corresponding saturated esters. The same steps gave Hexahydrophenyl acetic ester from Cyclohexanone, and the method appears to afford a general mode of preparation of acids from the lower aldehyde or ketone.

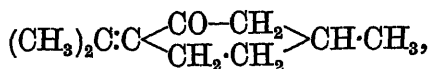
Zelinsky (*Ber.*, 1911, 44, 2305) converted Methyl Δ^1 -tetrahydroterephthalate into a mixture of Methyl hexahydroterephthalate and Methyl terephthalate at the ordinary temperature, using Palladium-black and Hydrogen.

Ethylenic Aldehydes can, under carefully adjusted conditions, be reduced to the corresponding saturated aldehyde, but simultaneously some reduction of the aldehyde to alcohol usually occurs. Propenyl aldehyde, $CH_2:CH \cdot CHO$, hydrogenated with Nickel at 160° C., yields mainly Propyl aldehyde (Henrard, *Chem. Zentr.*, 1907, (2), 1512). Crotonic aldehyde, hydrogenated with Nickel at 125° C., gives a yield of about 50 per cent. of Butyric aldehyde and 20 per cent. of Butyl alcohol. At higher temperatures, more alcohol is formed (Douris, *Bull. Soc. chim.*, 1911, (4), 9, 922).

Ethylenic Ketones can be hydrogenated to the corresponding saturated ketones, but usually not sufficiently rapidly to avoid some formation of secondary alcohol by simultaneous reduction of the keto-group.

Mesityl oxide $(CH_3)_2C:CH \cdot CO \cdot CH_3$, is hydrogenated by Nickel at 160–170° C. to Methyl isobutyl ketone, $(CH_3)_2CH \cdot CH_2 \cdot CO \cdot CH_3$, but some of the corresponding alcohol is formed, and some 2-Methyl pentane (Skita, *Ber.*, 1908, 41, 2938; Darzens, *C.R.*, 1905, 140, 152). Phorone, $(CH_3)_2C:CH \cdot CO \cdot CH:C(CH_3)_2$, is hydrogenated with Nickel at 160–170° C. quantitatively to Di-isobutyl ketone or Valerone. At 225° C., some of the corresponding secondary alcohol and saturated hydrocarbon are formed (Sabatier and Mailhe, *Ann. Chim. Phys.*, 1909, (8), 16, 79; Skita, *Ber.*, 1908, 41, 2938). Cyclic ketones con-

taining an ethylenic linkage can generally be hydrogenated without any attack on the keto-group, thus, Pulegone,



and Camphorone, $\text{CH}_3 \cdot \text{CH} \begin{array}{c} \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{C}:\text{C}(\text{CH}_3)_2$, by a rapid passage with Hydrogen over catalytic Nickel, the former at 140–160° C. and the latter at 130° C., are hydrogenated quantitatively to the dihydro-derivatives (Haller and Martine, *C.R.*, 1905, 140, 1298, and Godchot and Taboury, *C.R.*, 1913, 156, 470).

Unsaturated Ethers. Allyl ether, with excess of Hydrogen, over Nickel at 130–140° C., is reduced quantitatively to Propyl ether (Darzens, *C.R.*, 1907, 144, 328; *Bull. Soc. chim.*, 1907, 4, I, 179).

Safrole and isoSafrole, $\text{CH}_3 \cdot \text{CH}:\text{CH} \cdot \text{C}_6\text{H}_5 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \end{array} \text{CH}_2$, likewise give a dihydro-derivative, but reduction is not quantitative, and some meta-Propyl phenol is formed (Henrard, *Chem. Weekblad*, 1907, 4, 630).

Hydrogenation of Acetylenic Compounds. Simple homologues of Acetylene behave in the same way as Acetylene (Sabatier and Senderens, *C.R.*, 1902, 135, 87). α -Heptylidene with excess of Hydrogen over catalytic Nickel at 170° C. gives mainly normal Heptane, with small quantities only of higher hydrocarbons. Reduced Copper above 200° C. gives α -Heptylene, Diheptylene, and Triheptylene, as well as normal Heptane.

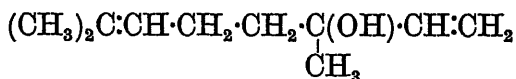
Phenyl acetylene, $\text{C}_6\text{H}_5 \cdot \text{C}:\text{CH}$, hydrogenated with Nickel at 180° C., gives Ethyl cyclohexane, with small quantities of Methylcyclohexane, due to rupture of the acetylenic linkage. Copper at 190–250° C. gives Phenyl ethylene and Ethyl benzene, but also Diphenyl butane, $\text{C}_6\text{H}_5(\text{CH}_2)_4 \cdot \text{C}_6\text{H}_5$, the yield of this under certain conditions reaching as much as 50 per cent. of theory.

Other unsaturated substances which have been reduced by the method of Sabatier and Senderens are the following:—

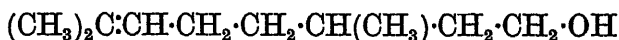
Trimethyl ethylene, $(\text{CH}_3)_2\text{C}:\text{CH} \cdot \text{CH}_3$; 2-Hexene; Caprylene (1-Octene); (Sabatier and Senderens, *C.R.*, 1902, 134, 1127). 2:2-Dimethyl 3-methylene pentane; 2-Ethyl 5-methyl hexene; 2-Nonene (Clark and Jones, *J. Amer. C.S.*, 1912, 34, 170; 1915, 37, 2536; Clark and Beggs, *ibid.*, 1912, 34, 54). Methyl propyl octene; 4-Cyclohexyl heptene; 1-Phenyl 2-propyl pentene (Murat and Amouroux, *J. Pharm. Chim.*, 1912, (7), 5, 473). 1:1:1-Diphenyl propene; 1:2:1-Diphenyl propene (Sabatier and Murat, *C.R.*, 1912, 155, 386). α -Pinene (Zelinsky, *Ber.*, 1911, 44, 2782). Citral; Ocimene or 2:6-dimethyl 2:5:7-octatriene,



from oil of basil; Geraniol or 2:6-Dimethyl 2:6-octadiene 8-ol, $(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3):\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ (giving 2:6-Dimethyl octanol, and a little of the hydrocarbon, 2:6-Dimethyl octane); Linalool or 2:6-Dimethyl 2:7-octadiene 6-ol,



(giving the same products); Citronellol,



(Enklaar, *Ber.*, 1908, 41, 2083, *Rec. trav. chim. Pays Bas*, 1908, 27, 411; Haller and Martine, *C.R.*, 1905, 140, 1298). Three Dimethyl cyclohexenes, obtained from the three corresponding Dimethyl cyclohexanols by catalytic dehydration (Sabatier and Mailhe, *Ann. Chim. Phys.*, 1907, (8), 10, 552). 1:2-Methyl ethyl cyclohexene (Murat, *Bull. Soc. chim.*, 1907, (4), I, 774). 1:1-Phenyl cyclohexene; 1:1-Cyclohexyl cyclohexene (Sabatier and Murat, *C.R.*, 1912, 154). Menthene and Camphene (Sabatier and Senderens, *C.R.*, 1901, 132, 1256). Tetrahydrobenzoic ethyl ester, $\text{C}_6\text{H}_5\cdot\text{COOC}_2\text{H}_5$; Cyclohexene acetic ethyl ester, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5$ (Darzens, *C.R.*, 1907, 144, 328). Terpineol (Haller and Martine,

C.R., 1905, 140, 1303). α -Thuyene, $\text{CH}_3\cdot\text{C}\begin{array}{c} \nearrow \text{CH}\cdot\text{CH}_2 \\ \searrow \text{CH}\cdot\text{CH}_2 \end{array}\text{C}\cdot\text{CH}(\text{CH}_3)_2$

(Zelinsky, *J. Russ. Phys. Chem. Soc.*, 1904, 36, 768), Oleic acid and Amyl oleate (Fokin, *J. Russ. Phys. Chem. Soc.*, 1906, 38, 419). Esters of Acrylic acid; Dimethyl acrylic ethyl ester; Oenanthylidene acetic ethyl ester, $\text{C}_6\text{H}_{13}\cdot\text{CH}:\text{CH}\cdot\text{COOC}_2\text{H}_5$; Methyl cinnamate, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COOCH}_3$; Phenyl isocrotonic ethyl ester; Ethyl Δ^8 -nonenoate, Undecenoic ethyl ester (made by distillation of castor oil *in vacuo*); Ethyl cinnamate; a series of $\beta\beta'$ -Methyl alkyl acrylic

esters of the type $\text{CH}_3\begin{array}{c} \text{R} \\ \diagup \end{array}\text{C}:\text{CH}\cdot\text{COOC}_2\text{H}_5$, made by condensing ketones, $\text{R}\cdot\text{CO}\cdot\text{CH}_3$, with Ethyl chloroacetate; $\Delta^{1:2}$ -Cyclohexene carboxylic ester, made from Cyclohexanone *via* the bisulphite compound and nitrile, using KCN, followed by hydrolysis with cold HCl to Hydroxycyclohexane carboxylic acid, and dehydration of the ethyl ester of this acid with P_2O_5 ; the ortho-, meta-, and para-Methyl homologues of $\Delta^{1:2}$ -Cyclohexene carboxylic ester, made similarly (Darzens, *C.R.*, 1907, 144, 328; *Bull. Soc. chim.*, 1907, (4), 1, 179). Methyl hexenone, $(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$, and natural Methyl heptenone (Darzens, *C.R.*, 1905, 140, 152). 3-Methyl 3-heptene 5-one; 2:4:8-Trimethyl 4-nonene 6-one; (Bodroux and Taboury, *C.R.*, 1909, 149, 422); Pulegone (Haller and Martine, *C.R.*, 1905, 140, 1298).

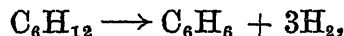
Hydrogenation of Aromatic Compounds

Benzene derivatives which are volatile and stable, and contain no catalytic poisons, can be hydrogenated to the corresponding Cyclohexane derivatives by means of catalytic Nickel at 170–220° C. When a Benzene derivative contains another grouping capable of reduction or hydrogenation, the following rules hold in almost all cases. 1. Since hydrogenation of the Benzene ring is one of the most difficult to accomplish, other reducible groupings are usually attacked first. 2. The aromatic nucleus is only hydrogenated by active Nickel, *i.e.*, reduced below 300° C. If it is desired to reduce the second group only, it can therefore be accomplished either by using slightly active Nickel (reduced above 300° C.) or another metal catalyst. 3. Using active Nickel the aromatic nucleus is in some measure always hydrogenated before reduction of the other group is complete.

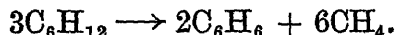
Hydrocarbons. When Hydrogen saturated at the ordinary temperature with Benzene vapour is passed over finely-divided Nickel, reduced from its oxide at a temperature below 300° C., hydrogenation of the Benzene commences at 70° C. As the temperature of the Nickel is raised, the speed of hydrogenation increases, and reaches a maximum at 180–200° C. At this temperature, Benzene can be almost completely converted into its hexahydro-derivative, Cyclohexane, identical with the main constituent of Caucasian petroleum,



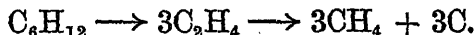
Partially hydrogenated Benzene derivatives are never formed. If Benzene is in excess in the original mixture the product consists of a mixture of Cyclohexane and unchanged Benzene (Sabatier and Senderens, *C.R.*, 1901, 132, 210). If the temperature is raised beyond 200° C., the reverse change, dehydrogenation of Cyclohexane to Benzene, commences,



and above 250° C. is accompanied by other and more destructive changes, such as



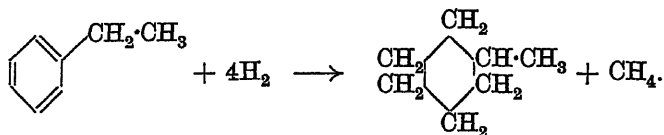
At 300° C. with Nickel, degradation is much more complete, Cyclohexane giving chiefly Carbon, which remains on the catalyst, and Methane. Sabatier and Senderens supposed that the Cyclohexane first split into Ethylene, which then decomposed in the manner we have described,



These reactions are general for aromatic hydrocarbons. The optimum temperature for hydrogenation is usually between 180° C. and 200° C., and at higher temperatures dehydrogenation and decomposition begin.

Sabatier and Senderens (*C.R.*, 1901, 132, 561, 1254) obtained high yields of the corresponding Cyclohexane hydrocarbons from the following homologues of Benzene: Toluene, the three Xylenes, Ethyl benzene, 1:3:5- and 1:3:4-Trimethyl benzenes (Mesitylene and Pseudocumene), 1-Methyl 4-ethyl benzene, Propyl benzene and 1-Methyl 4-isopropyl benzene.

The hydrogenation is almost quantitative in the cases of Benzene and the methyl derivatives, the sole product being the corresponding Cyclohexane, so long as the temperature is below 250° C. When, however, ethyl, propyl, or longer aliphatic chains are attached to the Benzene ring, small quantities of lower homologues are formed along with the principal product. Thus, Ethyl benzene gives a little Methyl cyclohexane, and Propyl benzene gives small quantities of both Ethyl and Methyl cyclohexanes,

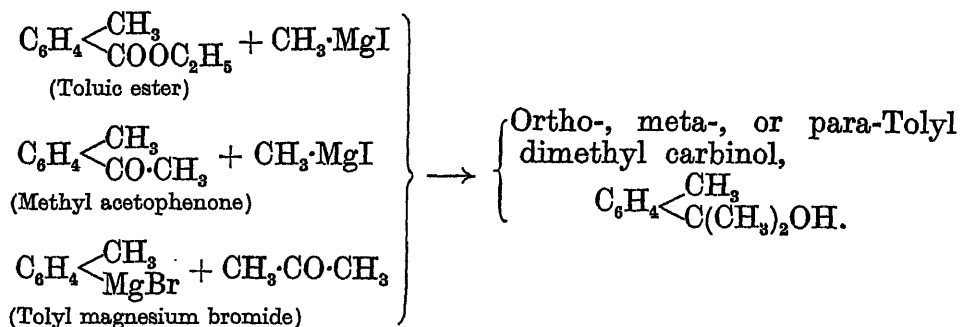


The longer the side-chain the greater is the tendency for this bye-reaction to occur. If there is a secondary branch in the side-chain, the bye-reaction is still more pronounced. For example, para-Cymene (Methyl para-isopropyl benzene), $\text{CH}_3\cdot\text{C} \begin{smallmatrix} \text{CH}\cdot\text{CH} \\ \text{CH}:\text{CH} \end{smallmatrix} \text{C}\cdot\text{CH} \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$, on hydrogenation gives approximately 66 per cent. of the normal product, para-Methyl isopropyl cyclohexane, and 12 per cent. each of the degradation products, para-Dimethyl cyclohexane and para-Methyl ethyl cyclohexane. As the temperature is raised beyond 200° C., this degradation becomes more marked.

Styrene, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}_2$, with active Nickel at 200° C. gives entirely Ethyl cyclohexane. If, however, Copper at 180° C. is used, or feebly active Nickel at 200° C., only the ethylenic grouping is reduced, and Ethyl benzene is the only product, whilst with Cobalt intermediate in activity between Copper and Nickel the product is a mixture of Ethyl benzene and Ethyl cyclohexane (Sabatier and Senderens, *C.R.*, 1901, 132, 1254).

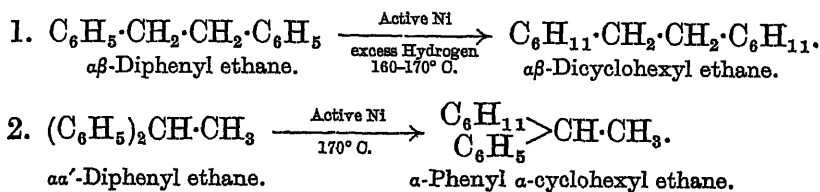
Partially reduced aromatic compounds, including many terpenes, are completely hydrogenated by Nickel to Cyclohexane derivatives. Thus Limonene, Sylvestrene, Terpinene, Menthene, and para-Cymene all produce 1-Methyl 4-isopropyl cyclohexane, and Terebenthene and l-Camphene give two isomeric hydrocarbons, $\text{C}_{10}\text{H}_{18}$.

Sabatier and Murat prepared the three Cymenes by Grignard's reaction, and from these, by catalytic hydrogenation, the three corresponding Menthanes. The steps may be represented as follows :—

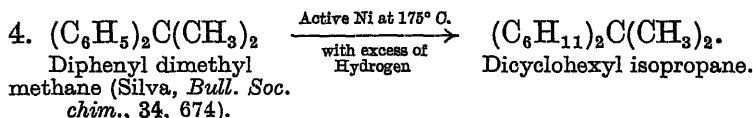
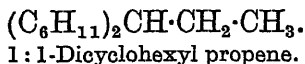
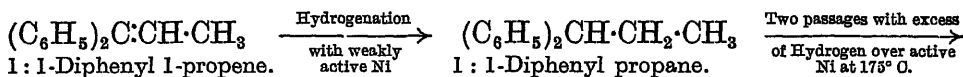
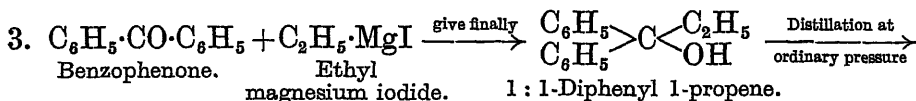
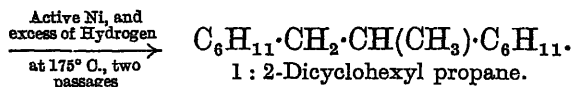
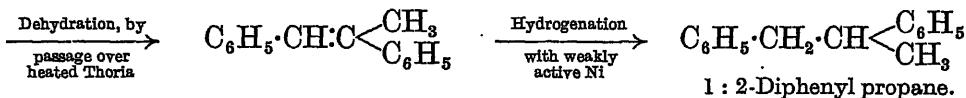
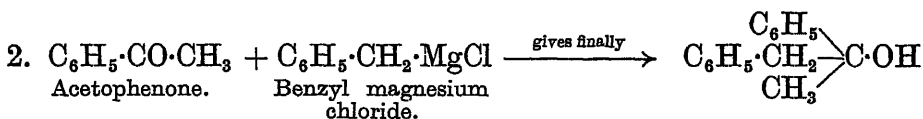
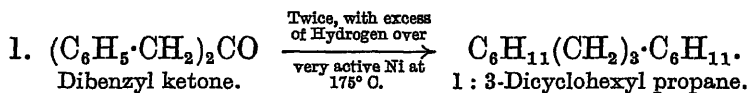


Mild catalytic dehydration of these tertiary alcohols gave the corresponding Cresyl propenes, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}:\text{CH}_2 \\ \diagup \\ \text{CH}_3 \end{array}$, which by hydrogenation with slightly active Nickel at 200–220° C. gave the corresponding Cymenes, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CH}(\text{CH}_3)_2 \end{array}$. Finally, hydrogenation of the Cymenes at 170° C. with active Nickel gave the three corresponding Menthanes (*C.R.*, 1913, 156, 184).

Eijkman (*Chem. Weekblad*, 1903, I, 7), and others, applied this method of hydrogenation to substances containing several aromatic nuclei. Diphenyl methane, $(\text{C}_6\text{H}_5)_2\text{CH}_2$, easily gave Dicyclohexyl methane $(\text{C}_6\text{H}_{11})_2\text{CH}_2$, and Diphenyl, $(\text{C}_6\text{H}_5)_2$, gave Phenyl cyclohexane, $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_{11}$. Sabatier and Murat (*C.R.*, 1912, 154, 1390), by using a large excess of Hydrogen and a very active Nickel at 160° C., further hydrogenated Phenyl cyclohexane to nearly pure Dicyclohexyl, $\text{C}_6\text{H}_{11}\cdot\text{C}_6\text{H}_{11}$. Godchot (*C.R.*, 1908, 147, 1057) hydrogenated Triphenyl methane, $\text{CH}(\text{C}_6\text{H}_5)_3$, to Dicyclohexyl phenyl menthane, $(\text{C}_6\text{H}_{11})_2\text{CH}\cdot\text{C}_6\text{H}_5$, and Tricyclohexyl methane, $(\text{C}_6\text{H}_{11})_3\text{CH}$, but could not isolate the former in a state of purity. Sabatier and Murat made the two possible Dicyclohexyl ethanes (*C.R.*, 1912, 154, 1771) and the four possible Dicyclohexyl propanes (*C.R.*, 1912, 155, 385). The steps may be indicated as follows :—



The further hydrogenation of this compound was more difficult, and required three successive passages with excess of Hydrogen over very active Nickel at 170° C., when $\alpha\alpha'$ -Dicyclohexyl ethane, $(C_6H_{11})_2CH \cdot CH_3$, was produced.



Attempts by Sabatier and Senderens to hydrogenate Tetraphenyl ethane, $(C_6H_5)_2CH \cdot CH(C_6H_5)_2$, with Nickel at 230 – 240° C. failed, however, to produce Tetracyclohexyl ethane. Scission of the molecule occurred, and the products were always Diphenyl methane and Dicyclohexyl methane (*C.R.*, 1914, 157, 1496).

Nickel is the only useful catalyst known for hydrogenation of the Benzene ring. According to Sabatier and Senderens, Cobalt and Platinum-black have a transitory action, lost in the case of Platinum very quickly. Spongy Platinum, Iron, and Copper are quite inert. The action of Platinum-black has been confirmed by Lunge and Akunoff (*Z. anorg. Chem.*, 1900, 24, 191), who found that when Hydrogen containing 5 to 8 per cent. of Benzene vapour was circulated over Platinum-black about 3 times at 100° C., a contraction

in volume occurred corresponding with the transformation of the Benzene into Cyclohexane, while Palladium-black gave a smaller contraction, and by Zelinsky (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 274), who hydrogenated Benzene, Toluene, the three Xylenes, and Ethyl benzene to the corresponding Cyclohexanes by the use of Platinum and Palladium-black.

Aromatic Alcohols. Catalytic Nickel hydrogenates the aromatic nucleus to the Cyclohexane ring, and at the same time eliminates the hydroxyl group. Thus Benzyl alcohol, $C_6H_5 \cdot CH_2OH$, is reduced to Toluene and Methyl cyclohexane, while para-Tolyl dimethyl carbinol, $CH_3 \cdot C_6H_4 \cdot C(CH_3)_2OH$, hydrogenated with Nickel at $150^\circ C.$, gives Menthane, $CH_3 \cdot C_6H_{10} \cdot CH(CH_3)_2$ (Smirnov, *J. Russ. Phys. Chem. Soc.*, 1909, 41, 1374). Other instances are given in connection with the reduction of aromatic aldehydes and ketones, which give only hydrocarbons, owing to the instability under hydrogenating conditions of the aromatic alcohols.

Aromatic Ethers. At $150^\circ C.$, or below, Nickel hydrogenates the Benzene ring. Thus Anisole, $C_6H_5 \cdot O \cdot CH_3$, gives Methyl cyclohexyl ether, $C_6H_{11} \cdot O \cdot CH_3$, and the Methyl ethers of the three Cresols give the corresponding Methyl cyclohexyl methyl ethers, $CH_3 \cdot C_6H_{11} \cdot O \cdot CH_3$. Phenetole, $C_6H_5 \cdot O \cdot C_2H_5$, likewise gives Ethyl cyclohexyl ether, $C_6H_{11} \cdot O \cdot C_2H_5$ (Brunel, *Ann. Chim. Phys.*, 1905, (8), 6, 205; Sabatier and Senderens, *Bull. Soc. chim.*, 1905, (3), 33, 616).

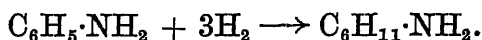
Aromatic Acids, such as Benzoic acid, cannot be hydrogenated to the Cyclohexane carboxylic acid. Active Nickel at 170 – $180^\circ C.$, with Benzoic acid, gives small quantities of Cyclohexane and traces of Cyclohexane carboxylic acid, but soon ceases to exert any action whatever (Sabatier and Murat, *C.R.*, 1912, 154, 923).

Esters of Aromatic Acids, on the other hand, hydrogenate smoothly to esters of the corresponding Cyclohexane carboxylic acids (Sabatier and Murat, *loc. cit.*). At 170 – $200^\circ C.$, with Nickel, the Methyl, Ethyl, isoButyl and isoAmyl esters of Benzoic acid give the corresponding Cyclohexane carboxylic esters, which saponify to give Cyclohexane carboxylic acid in high yield. Esters of the three Toluic acids give in the same way the corresponding Methyl cyclohexyl carboxylic esters, $CH_3 \cdot C_6H_{10} \cdot COOC_2H_5$.

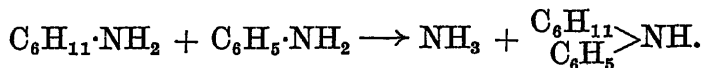
Benzene Substituted Aliphatic Esters. Esters of Phenyl acetic acid, $C_6H_5 \cdot CH_2 \cdot COOH$, are hydrogenated at 170 – $185^\circ C.$ in contact with Nickel, and give the corresponding Cyclohexyl acetic esters (Sabatier and Murat, *C.R.*, 1913, 156, 424). The numerous esters prepared each gave on saponification a high yield of Cyclohexyl acetic acid. Esters of β -Phenyl propionic acid, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot COOH$, likewise gave the esters of β -Cyclohexyl propionic acid (Sabatier and Murat, *C.R.*, 1913, 156, 751).

Aromatic Amines. In presence of catalytic Nickel, at $190^\circ C.$,

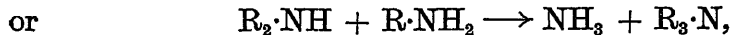
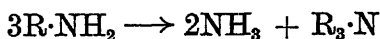
aromatic amines are hydrogenated to the corresponding cyclohexylamines. For instance, with Aniline,



The reaction does not, however, stop at this stage, since primary amines in contact with a heated catalyst interact to form Ammonia and secondary amines,



Tertiary amines which might be formed in the same way,

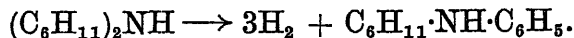


usually are not formed in appreciable quantity in the hydrogenation of aromatic amines. [*N.B.*—The tertiary amine is commonly the main product when aliphatic amines are prepared by reduction of Oximes, Nitriles, etc.]

Hydrogenation of Aniline therefore leads to the formation of Cyclohexylamine, $\text{C}_6\text{H}_{11}\cdot\text{NH}_2$, Dicyclohexylamine, $(\text{C}_6\text{H}_{11})_2\text{NH}$, and Cyclohexylaniline, $\text{C}_6\text{H}_{11}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, which are obtained in approximately equal quantities, and Ammonia. A trace of Diphenylamine, $(\text{C}_6\text{H}_5)_2\text{NH}$, is also formed (Sabatier and Senderens, *C.R.*, 1904, 138, 457, 1257).

Cyclohexylamine, the normal product, is identical with the compound obtained by Baeyer by reducing Cyclohexanone oxime (*Ann.*, 278, 88) and by Markownikov by reducing Nitro cyclohexane (*Ann.*, 1898, 302, 1). It is a colourless liquid of strong ammoniacal smell, and, like the aliphatic amines, a strong base, easily absorbing Carbon dioxide from air. Its boiling point is 135° C. at 760 mm.

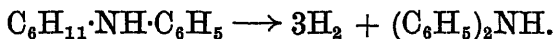
Dicyclohexylamine is a colourless liquid with a rather less strong ammoniacal smell than Cyclohexylamine. The boiling point is 145° C. at 30 mm., or 250° C. at 760 mm., with slight decomposition into Cyclohexylaniline,



Pure Dicyclohexylamine solidifies on cooling to prismatic crystals which melt at 20° C. The base is a strong one, but the carbonate formed by absorption of Carbon dioxide completely dissociates in air.

Cyclohexylaniline is a yellow liquid with a faint odour boiling

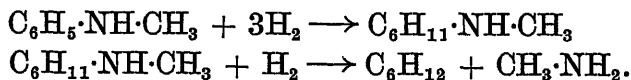
at 171° C. at 30 mm., and at 275° C. at 760 mm., with slight decomposition into Diphenylamine,



Pure Cyclohexylaniline crystallises on cooling and the solid melts at 10° C. As a base, it is much weaker than Mono- or Dicyclohexylamine, resembling Aniline, and does not easily form a carbonate.

Using a very active Nickel catalyst at the lowest possible temperature, 160–180° C., the secondary products, Dicyclohexylamine and Cyclohexylaniline, are formed in much smaller quantity, and nearly pure Cyclohexylamine can be obtained. Prolonged action of Hydrogen on Diphenylamine in presence of catalytic Nickel at 190–210° C. gives a liquid containing Cyclohexylaniline and Dicyclohexylamine, but mostly Benzene, Aniline, and Cyclohexylamine.

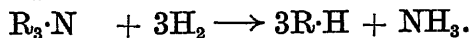
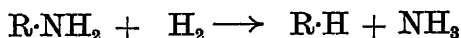
Homologues of Aniline likewise give Cyclohexylamine derivatives. When substituents are attached to the Benzene nucleus, a mixture of three products is formed as with Aniline. Thus meta-Toluidine at 200–210° C. gives the corresponding Methyl cyclohexylamine, b. p. 150° C., 760 mm. Di-methylcyclohexylamine ($\text{CH}_3\cdot\text{C}_6\text{H}_{10}$)₂NH, b. p. 145° C., 20 mm., and Methyl cyclohexyl meta-Toluidine, b. p. 175° C., 20 mm. When, however, an aromatic amine is substituted in the amido-group, this mixture of products is not formed. Secondary or tertiary aromatic amines (Alkyl anilines) are directly hydrogenated to the corresponding pure Alkyl cyclohexylamines, and the action is often easier than with Aniline. At the same time, a secondary reaction sometimes occurs, as with Methylaniline, which on hydrogenation at 160–170° C. gives mainly Cyclohexyl methylamine, but a certain amount of Methylamine and Cyclohexane,



Using Ethyl aniline, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{C}_2\text{H}_5$, Diethylaniline, $\text{C}_6\text{H}_5\cdot\text{N}(\text{C}_2\text{H}_5)_2$, or Dimethyl aniline, $\text{C}_6\text{H}_5\cdot\text{N}(\text{CH}_3)_2$, and catalytic Nickel at 160–180° C., this bye-reaction does not occur, and good yields of the Cyclohexyl derivatives are obtained (Sabatier and Senderens, *C.R.*, 1904, 138, 1257; Darzens, *ibid.*, 1909, 149, 1001).

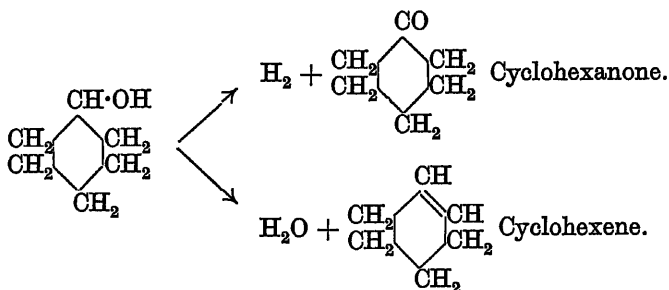
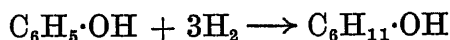
Benzene Substituted Aliphatic Amines. Sabatier and Mailhe (*C.R.*, 1911, 153, 160) hydrogenated pure Benzylamine, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{NH}_2$, made by passing a mixture of Benzyl alcohol vapour and Ammonia over heated Thoria, and obtained Hexahydrobenzylamine and Dihexahydrobenzylamine. Benzylamine as made by the usual chemical methods could not be hydrogenated to the hexahydro-derivative, but gave only Toluene and Ammonia, the presence of a trace of halogen being probably responsible for this difference.

Hydrogenation of Amines at High Temperatures. All amines, aromatic or aliphatic, when passed with Hydrogen over catalytic Nickel at temperatures above 220°C ., lose Ammonia and are converted into hydrocarbons as follows :—



At still higher temperatures, the degradation proceeds to completion.

Phenols. Phenol and its derivatives are easily hydrogenated to the corresponding Cyclohexanol derivatives when passed with excess of Hydrogen over active Nickel at temperatures between 180°C . and 230°C . Using Phenol at the lower temperature, 180°C ., Cyclohexanol is the main product, but in addition to a little unchanged Phenol, the ketone (Cyclohexanone) and the unsaturated hydrocarbon (Cyclohexene) are also obtained by dehydrogenation or dehydration, respectively, of the Cyclohexanol :—



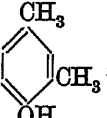
As the temperature of the catalyst is raised above 180°C ., formation of Cyclohexanone increases, and at 230°C . considerable quantities are formed (Sabatier and Senderens, *C.R.*, 1903, 137, 1025). A mixture of Cyclohexanol and Cyclohexanone produced in this way distills between 155°C . and 165°C ., and therefore cannot be easily resolved into its constituents by fractionation. Pure Cyclohexanol or pure Cyclohexanone can be obtained from the mixture as follows: For Cyclohexanol, the product obtained by hydrogenation at 180°C . is passed again with Hydrogen over active Nickel at 150 – 170°C . Unchanged Phenol and Cyclohexanone are thereby reduced completely to Cyclohexanol.

Cyclohexanol boils at 161°C ., solidifies when cooled, and remelts at 16°C . The product obtained corresponds with the substance made in other ways by Baeyer (*Ann.*, 278, 88), and Markownikov.

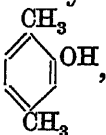
To obtain pure Cyclohexanone, the mixture obtained by hydro-

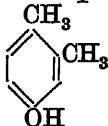
genation at 220–230° C. is passed alone over a dehydrogenating catalyst, *e.g.*, Copper, at 330° C. Cyclohexanol is almost completely converted into Cyclohexanone, which can, if desired, be purified completely by way of its bisulphite compound. Cyclohexanone is a colourless liquid with an odour resembling that of Camphor. It boils at 155.5° C., and the product obtained as described is identical with Baeyer's (*loc. cit.*) and Markownikov's.

Homologues of Phenol behave more or less similarly, giving varying quantities of the Cyclohexanol, Cyclohexanone, and Cyclohexene. Thus, direct hydrogenation effects the following reactions: Ortho- and para-Cresols with Nickel at 200–225° C. give 90 per cent. yields of the corresponding Methyl cyclohexanols, and traces only of the Methyl cyclohexanone, easily removable by shaking with a strong solution of Sodium bisulphite. Meta-cresol gives with Nickel at 220° C. a mixture of Methyl cyclohexanol and Methyl cyclohexanone, from which the pure compounds can be obtained, as in the case of Phenol, by hydrogenating with Nickel at 150° C., or dehydrogenating with Copper at 330° C. (Sabatier and Mailhe, *C.R.*,

1905, 140, 350). 1:3:4-Xylenol, , with Nickel at 190–200° C.,

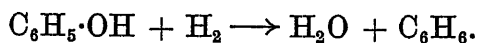
gives the corresponding Dimethyl cyclohexanol as the chief product, with a little Dimethyl cyclohexanone and Dimethyl cyclohexene.

1:4:2-Xylenol, , under the same conditions, gives a 90 per cent. yield of 1:4-Dimethyl cyclohexanol, and about 10 per

cent. of 1:4-Dimethyl cyclohexanone. 1:2:4-Xylenol, ,

on the other hand, is reduced to a mixture containing up to 60 per cent. of ortho-Xylene, while of the remainder 30 per cent. is 1:2-Dimethyl cyclohexanol and 10 per cent. is 1:2-Dimethyl cyclohexanone (Sabatier and Mailhe, *C.R.*, 1906, 142, 553).

At temperatures above 250° C., catalytic Nickel in presence of Hydrogen slowly reduces Phenol to Benzene,



As the temperature is raised, more extensive decomposition sets in, the Benzene formed undergoing degradation in the ways already described. Homologues of Phenol are similarly decomposed, first into the hydrocarbon, and then more completely.

Polyphenols. On account of their lower stability, addition of Hydrogen to polyphenols to give the corresponding polyhydroxy-cyclohexanes is often difficult. About 200° C., under the influence of catalytic Nickel, hydroxy-groups are easily eliminated, leading to the formation of Phenol and Benzene, together with Cyclohexanol and Cyclohexane as secondary products. Only in cases where hydrogenation is possible at a low temperature, 150° C. or lower, can the polyhydroxy-cyclohexane derivatives be obtained (Sabatier and Senderens, *Ann. Chim. Phys.*, 1905, (8), 4, 429).

Pyrogallol with very active Nickel at 120–130° C. gives 1 : 2 : 3-Cyclohexatriol, and Catechol at 130° C. gives cis-1 : 2-Cyclohexadiol without any of the trans-isomer (Sabatier and Mailhe, *C.R.*, 1908, 146, 1193). Hydroquinone with Nickel at 130° C. gives cis-1 : 4-Cyclohexadiol without any trans-isomer, but at 160–170° C. a mixture of Phenol, Cyclohexanol, and cis- and trans-1 : 4-Cyclohexadiols is obtained. Traces only of a definite compound could be obtained from Resorcinol on account of its low volatility. The amount was insufficient to identify as cis-1 : 3-Cyclohexadiol.

The following Benzene derivatives also have been hydrogenated to the corresponding Cyclohexane derivatives: Diphenyl butane, $C_6H_5(CH_2)_4C_6H_5$ (Sabatier and Murat, *C.R.*, 1913, 156, 1430); para-Butyl phenol, Methyl butyl phenol, Dimethyl butyl phenol (Darzens and Rost, *C.R.*, 1911, 152, 607); Diethyl phenol (Henderson and Boyd, *J.C.S.*, 1911, 99, 2159); Thymoquinol, $C_6H_2(CH_3)(C_3H_7)(OH)_2$ (Henderson and Sutherland, *J.C.S.*, 1910, 97, 1616); Thymol, Carvacrol (Brunel, *C.R.*, 1903, 137, 1268).

Hydrogenation of Polymethylenes and their Derivatives

Cyclopropane or Trimethylene, $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH}_2 \end{array}$, is easily hydrogenated in presence of Nickel at temperatures between 80° C. and 180° C. to Propane (Willstätter and Bruce, *Ber.*, 1907, 40, 4456; Willstätter and Kametaka, *Ber.*, 1908, 41, 1480). Similarly, Dimethyl cyclopropyl ethylene, $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > C(CH_3)_2$, is hydrogenated below 100° to Methyl pentane, $(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot CH_3$ (Zelinsky, *Ber.*, 1907, 40, 4743).

Zelinsky synthesised the dicyclic cyclopropane derivative, "Spiro-cyclane," $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > C < \begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array}$ (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1870, 1873; *Ber.*, 1912, 46, 160, 163), and showed that it could be hydrogenated in stages according to the catalyst used. With Nickel at 200° C., complete reduction to Pentane always occurred. Palladium enabled Ethyl trimethylene to be obtained as the sole product, while

with Platinum, first Ethyl trimethylene and finally Pentane could be isolated (Zelinsky and Schtscherbak, *J. Russ. Phys. Chem. Soc.*, 1912, 44, 275, 1880; *Ber.*, 1912, 46, 168).

Cyclobutane or Tetramethylene, $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array}$, is hydrogenated at 180° C. with catalytic Nickel to Butane.

Cyclobutene, $\begin{array}{c} \text{CH}_2 \cdot \text{CH} \\ | \quad | \\ \text{CH}_2 \cdot \text{CH} \end{array}$, at 100° C. gives Cyclobutane, and then at 180° C. Butane (Willstätter and Bruce, *Ber.*, 1907, 40, 3979, 4456).

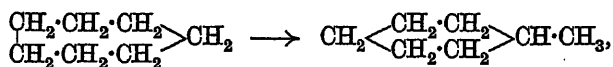
Cyclopentane and Cyclohexane are not hydrogenated to Pentane or Hexane and undergo no reaction at all in contact with catalytic Nickel except the usual degradative changes at a high temperature. Incompletely hydrogenated Cyclopentane and Cyclohexane derivatives, however, are easily reduced to the corresponding completely hydrogenated compound. Thus, Cyclopentadiene, $\begin{array}{c} \text{CH} \cdot \text{CH} \\ | \quad | \\ \text{CH} \cdot \text{CH} \end{array} > \text{CH}_2$,

is easily reduced to Cyclopentane (Eijkman, *Chem. Weekblad.*, 1903, I, 7) and Cyclohexene, $\text{CH} < \begin{array}{c} \text{CH} \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CH}_2$, or Cyclohexadiene,

$\text{CH} < \begin{array}{c} \text{CH} \cdot \text{CH}_2 \\ | \quad | \\ \text{CH} \cdot \text{CH} \end{array} > \text{CH}_2$, to Cyclohexane below 180° C. Substituted

Cyclopentenes and Cyclohexenes can similarly be hydrogenated easily to the corresponding Cyclopentane or Cyclohexane derivatives, and if a second reducible group is present in a Cyclopentene or Cyclohexene compound saturation of the ring can often be effected selectively, leaving the other grouping unaffected. Thus Cyclohexenyl methyl ketone, $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_9$, is easily hydrogenated to Cyclohexyl methyl ketone, $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_6\text{H}_{11}$ by means of Nickel at 160° C., the keto-group being quite unattacked (Darzens and Rost, *C.R.*, 1910, 151, 758). Carvone, however, cannot be hydrogenated to the dihydro-derivative without some reduction of the keto-group, a mixture of Dihydrocarvols resulting (Haller and Martine, *C.R.*, 1905, 140, 1302).

Cycloheptane and Cyclo-octane are attacked only very slowly by Hydrogen in presence of catalytic Nickel at temperatures below 200° C. At 200–250° C., the rings undergo isomeric change to the stabler Cyclopentane and Cyclohexane rings, Methyl cyclohexane and Dimethyl cyclohexane, respectively, being the main products, with varying quantities of isomeric alkylated Cyclopentanes (Willstätter and Kametaka, *Ber.*, 1908, 41, 1480). Thus, with Nickel at 235° C., Cycloheptane gives mainly Methyl cyclohexane,



but small amounts of Dimethyl cyclopentanes are also formed. At 250° C., aromatic hydrocarbons begin to appear in consequence of dehydrogenation, which, as Sabatier and Senderens found, commences about 240° C.

Cyclo-octane, as prepared by the method of Willstätter and Veraguth (*Ber.*, 1907, 40, 957), in contact with Nickel at 205–210° C. yields chiefly Dimethyl cyclohexanes, apparently with small quantities of alkylated cyclopentanes.

Dicyclo-octane, C_8H_{14} , a Cyclo-octane derivative with a bridged linkage, prepared by Willstätter and Veraguth by reduction of Dicyclo-octene, on hydrogenation with Nickel at 200–205° C. gives a mixture identical with that obtained from Cyclo-octane, which is probably an intermediate product, formed by reduction of the bridged linkage.

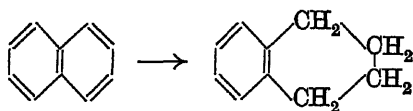
Partially hydrogenated Cycloheptane and Cyclo-octane rings are easily hydrogenated completely. Thus, below 180° C., in contact with Nickel, Cycloheptene and the Cycloheptadienes give Cycloheptane, and Cyclo-octadiene gives Cyclo-octane (Willstätter and Kametaka, *Ber.*, 1908, 41, 1480; Willstätter and Veraguth, *ibid.*, 1907, 40, 957; Willstätter and Waser, *ibid.*, 1911, 44, 3444).

The experiments of Willstätter and his collaborators illustrate very clearly the relative stabilities of the Polymethylenes. In presence of excess of Hydrogen, and in contact with active Nickel, the saturated Polymethylenes behave as follows:—

Ethylene commences to form Ethane at 30° C.; Cyclopropane commences to form Propane at 80° C.; Cyclobutane commences to form Butane at 180° C.; Cyclopentane and Cyclohexane are stable; Cycloheptane and Cyclo-octane isomerise to stabler cyclic structures at temperatures between 200° C. and 250° C. The order of stability is very clearly shown, and is in complete accord with the indications of numerous other reactions which provided the evidence upon which Baeyer founded his "Strain Theory."

Hydrogenation of Fused Aromatic Rings

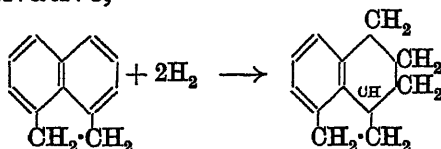
Naphthalene. When Naphthalene vapour is passed with excess of Hydrogen over catalytic Nickel at 200° C., Tetrahydronaphthalene is formed,



(Sabatier and Senderens, *C.R.*, 1901, 132, 1257). Leroux (*C.R.*, 1904, 139, 672) further hydrogenated Tetrahydronaphthalene. Using excess of Hydrogen, and passing the vapour several times over very active Nickel at 175° C., Decahydronaphthalene was obtained.

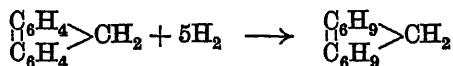
α -Naphthol and β -Naphthol, by several successive hydrogenations with very active Nickel, first at 170° C., then at 135–150° C., also gave the decahydro-derivatives, $C_{10}H_{17}\cdot OH$ (*C.R.*, 1905, 140, 590; 141, 953. *Ann. Chim. Phys.*, 1911, (8), 21, 483).

Acenaphthene, hydrogenated with Nickel at 210–230° C., forms the tetrahydro-derivative,



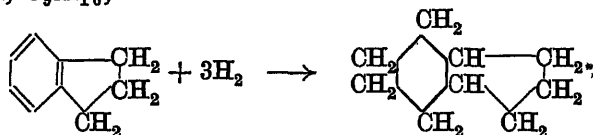
(Sabatier and Senderens, *C.R.*, 1901, 132, 1257; Godchot, *Bull. Soc. chim.*, 1908, (4), 3, 529).

Fluorene, hydrogenated with Nickel at 150° C., forms Decahydro-fluorene,



(Schmidt and Mezger, *Ber.*, 1907, 40, 4566).

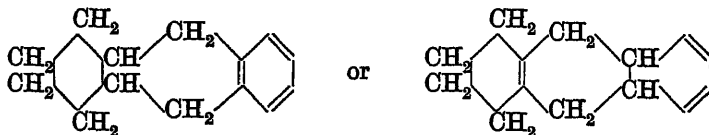
Hydrindene, hydrogenated with Nickel, gives a saturated dicyclic hydrocarbon, C_9H_{16} ,



(Eijkman, *Chem. Weekblad.*, 1903, I, 7).

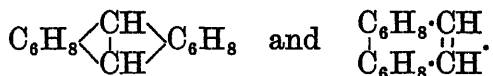
Anthracene. The tendency of metal catalysts to hydrogenate at lower temperatures and dehydrogenate at higher is clearly shown in the cases of Anthracene and Phenanthrene, where the more highly hydrogenated derivatives can only be obtained by working with catalysts of the highest degree of activity at the lowest possible temperature. The discrepant results obtained by different investigators, especially in hydrogenation of Phenanthrene, are probably due to the differences in activity of their catalysts.

Godchot (*Ann. Chim. Phys.*, 1907, (8), 12, 468) hydrogenated Anthracene with the most active Nickel he was able to obtain, formed by reduction of the oxide at 255–260° C. With excess of Hydrogen, and the catalyst at 260° C., he obtained Tetrahydroanthracene, $C_{14}H_{14}$, and at 200–205° C. Octahydroanthracene, $C_{14}H_{18}$. Powerfully active Nickel and several passages over the catalyst were necessary. Of the two possible formulæ for Octahydroanthracene,



Godchot preferred the former, since oxidation with alkaline permanganate readily gave Phthalic acid (*Bull. Soc. chim.*, 1907, (4), 1, 121).

Both formulæ were, however, disproved by Schroeter (*Brennstoff Chem.*, 1920, 1, 39). By heating Tetrahydronaphthalene to 30—40° C., with 1 per cent. of anhydrous Aluminium chloride, 30 per cent. was converted into a mixture of Octahydroanthracene and Octahydrophenanthrene, identical with the octahydro-derivatives formed by hydrogenation of Anthracene and Phenanthrene, respectively. Synthesis established that the true constitutions of these substances were



Perhydroanthracene, $\text{C}_{14}\text{H}_{24}$, was prepared by Godchot by hydrogenating Octahydroanthracene with Nickel at 175—180° C. The catalyst was used on the same day that it was prepared, in order that its activity might be a maximum. Older preparations gave a mixture of Perhydro- and Dodecahydro-anthracene, $\text{C}_{14}\text{H}_{22}$ (*Bull. Soc. chim.*, 1907, (4), 1, 724), which were separated by crystallisation from Alcohol. The former is a solid, melting at 88° C., while the latter is an oil, boiling at 145—150° C. at 15 mm. pressure.

Phenanthrene. Breteau (*C.R.*, 1905, 140, 942) obtained a mixture of Hexahydro- and Octahydro-phenanthrenes by hydrogenating Phenanthrene with a Nickel catalyst at 200° C. The two products were separated by fractional distillation, the former, $\text{C}_{14}\text{H}_{16}$, boiling at 305—307° C. (760 mm.) or 165—167° C. (13 mm.), and the latter, $\text{C}_{14}\text{H}_{18}$, at 280—285° C. (760 mm.) or 123—124° C. (13 mm.).

Schmidt and Mezger (*Ber.*, 1907, 40, 4240), however, state that with Nickel at 200° C. they obtained only Dihydrophenanthrene, $\text{C}_{14}\text{H}_{12}$.

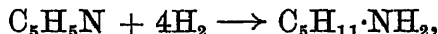
Padoa and Fabris (*Gazz.*, 1909, 39, 333) claim yet different results. With Nickel at 200° C., a mixture of Dihydrophenanthrene (solid) and Tetrahydrophenanthrene (liquid) was obtained, while with the catalyst at 175° C. they obtained Dodecahydrophenanthrene, $\text{C}_{14}\text{H}_{22}$.

Hydrogenation of Heterocyclic Ring Compounds

Pyrrole vapour, passed with Hydrogen over Nickel, reduced from its carbonate at 350° C., gave at 180—190° C., (a) Pyrrolidine in a yield of about 25 per cent. of theory, (b) Ammonia, (c) unchanged Pyrrole, (d) a hydrogenated Indol derivative, probably Hexahydro-indoline (Padoa, *Atti R. Accad. Lincei*, 1906, (V), 15, I, 219; *Gazz.*, 1906, 36, 317).

Pyridine. Sabatier and Mailhe (*C.R.*, 1907, 144, 784) found that Pyridine and Hydrogen in contact with catalytic Nickel reacted

only slowly, and that Piperidine was not formed. At 160° C. upwards, the Pyridine ring opened and Amylamine was slowly produced,

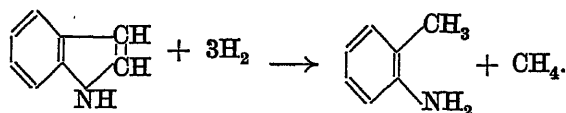


while at 220° C. the Amylamine was reduced to Pentane and Ammonia.

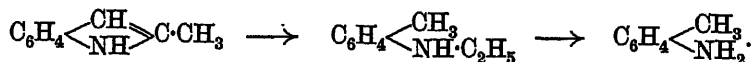
More recently, Padoa has reinvestigated the hydrogenation of Pyridine (*Atti R. Accad. Lincei.*, 1907, (V), 16, I, 818). Pyridine vapour and Hydrogen with Nickel at 180–250° C. reacted very slowly, giving traces of secondary bases (possibly including Piperidine) and a non-basic compound with the properties of the Pyrroles. The yield of both products was too small for complete identification. Since Piperidine contained the Hydrogen necessary for this transformation, Padoa sought to obtain larger quantities by passing this compound alone over Nickel at 180–250° C. The products were Pyridine, Pyrrole compounds in somewhat larger quantities than before, but still insufficient to examine, a secondary base, $\text{C}_{10}\text{H}_{21}\text{N}$, and an oily base, $\text{C}_{14}\text{H}_{28}\text{N}_2$, possibly Dipiperidyl butane.

More recently, Zelinsky and Borisov have hydrogenated Pyridine to Piperidine by using Platinised asbestos catalyst at 150° C. Palladised asbestos is rather more active, but quickly becomes poisoned by use. At 250° C., both catalysts induce dehydrogenation of Piperidine, after which they are quite inactive for hydrogenation (*Ber.*, 1924, 57 B, 150).

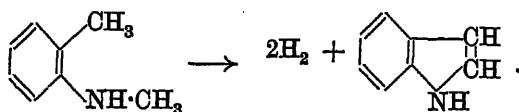
Indol. The hydrogenating and dehydrogenating actions of catalytic Nickel are illustrated again in the case of Indol, but in an unusual manner (Padoa and Carrasco, *Atti R. Accad. Lincei.*, 1906, (V), 15, I, 699). Passed with Hydrogen over catalytic Nickel at 200° C., Indol loses an atom of Carbon, and is hydrogenated, forming ortho-Toluidine as the main product,



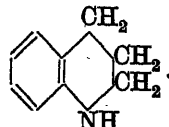
Likewise, α -Methylindol gives ortho-Toluidine. The action would appear to be



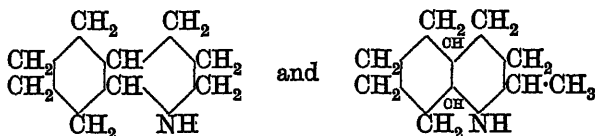
The reverse change, dehydrogenation, at higher temperatures, is shown by passing the vapour of Methyl ortho-Toluidine over Nickel at 300–330° C., when Indol is formed,



Quinoline. When hydrogenated with highly active Nickel at 160–180° C., Quinoline gives the tetrahydro-derivative,

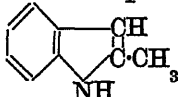


No Indol derivatives are formed (Darzens, *C.R.*, 1909, 149, 1001). At lower temperatures, with very active Nickel, Sabatier and Murat obtained from Quinoline, and from Quinaldine, the corresponding Decahydro-derivatives,

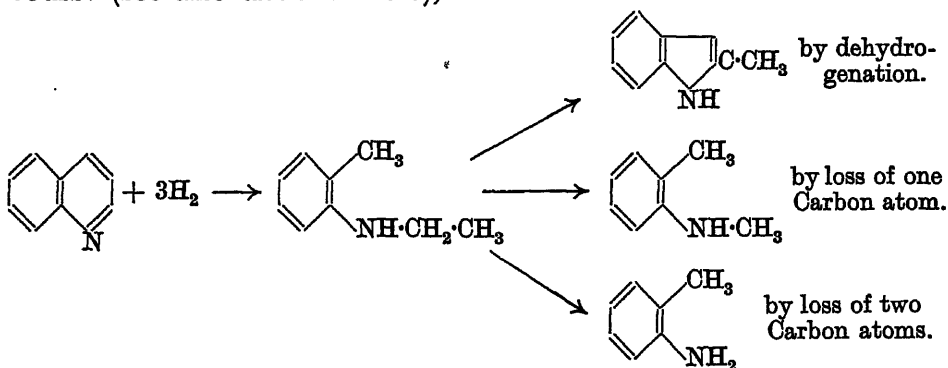


(*C.R.*, 1914, 158, 309).

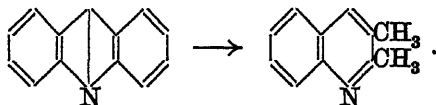
Padoa and Carughi (*Atti R. Accad. Lincei*, 1906, (V), 15, II, 113) hydrogenated Quinoline at higher temperatures. With reduced Nickel at 260–280° C., Quinoline vapour and Hydrogen gave a

mixture of 2-Methyl indole, , Methyl ortho-Toluidine

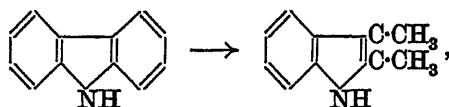
and ortho-Toluidine. The reaction probably takes the following course (see also under Indole),



Acridine was hydrogenated at a high temperature by Padoa and Fabris (*Atti R. Accad. Lincei*, 1907, (V), 16, I, 921) in the same way as Padoa and Carughi hydrogenated Quinoline. With catalytic Nickel at 250–270° C., 2:3-Dimethyl quinoline was formed instead of a Methyl carbazole, as would be expected by analogy with Quinoline:

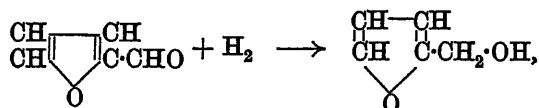


Carbazole. Padoa and Chiaves (*Gazz.*, 1907, **38**, I, 236) hydrogenated Carbazole with Hydrogen at 16–18 atmospheres pressure in presence of Nickel at 200–220° C. for 12 to 18 hours. The Carbazole was partially reduced to an Indol derivative, probably $\alpha\beta$ -Dimethyl indol,

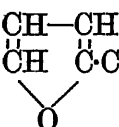


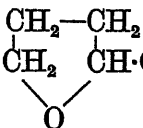
with a small amount of an unidentified base as a bye-product.

Furane. Padoa and Ponti (*Atti R. Accad. Lincei*, 1906, (V), 15, II, 610) showed that when Furfuraldehyde is passed with excess of Hydrogen over catalytic Nickel at about 190° C. mainly Furfuryl alcohol is obtained:



and small quantities of more highly hydrogenated bodies. In order to obtain these latter compounds in greater quantity, Furfuryl alcohol was hydrogenated in the same way. The products were

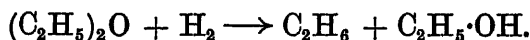
chiefly 2-Methyl furane: , but also 2-Methyl tetrahydro-

furane, , α -Methyl *n*-butyl alcohol, and Methyl propyl ketone.

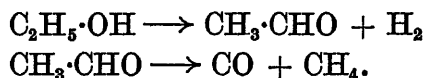
When Furfuraldehyde vapour alone was passed over catalytic Nickel at 270° C., Carbon monoxide was eliminated and Furane was formed (compare Benzaldehyde).

Hydrogenation of Ethers and Alcohols

Ethers are not easily reduced, and no action takes place with Hydrogen in contact with catalytic Nickel below about 250° C. At this temperature, the molecule is split into the corresponding Alcohol and Hydrocarbon,



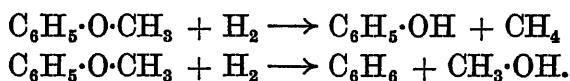
The Alcohol is in part further acted upon, forming Aldehyde, Methane, and Carbon monoxide,



Aromatic ethers behave similarly. At 150–180° C., the Benzene nucleus is hydrogenated in the normal manner. At higher temperatures, rupture of the molecule takes place, at the same time giving Cyclohexane,



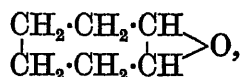
At still higher temperatures (300° C.), hydrogenation is completely suppressed and the products are Phenol, Benzene, and aliphatic hydrocarbons,



The Methyl alcohol shown in the last equations does not appear as such in the product, but is completely decomposed.

Oxides. Ethylene oxide when passed with Hydrogen over reduced Nickel at 125–150° C. gives Acetaldehyde, with a small quantity of Crotonaldehyde. The Nickel therefore catalyses the isomerisation of Ethylene oxide to Acetaldehyde before promoting hydrogenation to alcohol (Sabatier and Durand, *C.R.*, 1926, 182, 826).

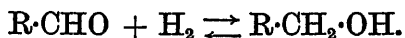
The Cyclohexadio oxide,



in a similar way, with Hydrogen and Nickel, at 160° C., gives a quantitative yield of Cyclohexanol (Brunel, *Ann. Chim. Phys.*, 1905, (8), 6, 237).

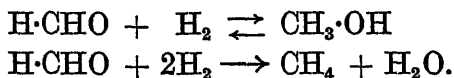
Reduction of Aldehydes

Under suitable conditions, aliphatic aldehydes can be reduced almost quantitatively to the corresponding primary alcohols (Sabatier and Senderens, *C.R.*, 1903, 137, 301). Nickel, reduced at a low temperature, is the best catalyst, since the greater its activity the lower is the temperature at which it is effective. The reverse change, dehydrogenation, which usually prevents complete reduction, is thereby minimised,



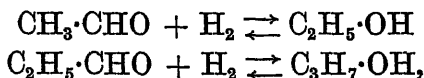
Other metals, which require a higher temperature than Nickel, are therefore less satisfactory catalysts.

Formaldehyde hydrogenated with active Nickel at 90° C. gives Methyl alcohol and some Methane,



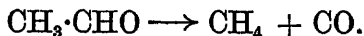
Solid Trioxymethylene is, however, deposited on the catalyst and its activity at 90° C. soon becomes very slight. This cannot be avoided by raising the temperature, since the reaction leading to Methane formation then becomes more pronounced.

In contact with active Nickel at 140° C., Acetaldehyde and Propionic aldehyde undergo quantitatively the reactions represented by



the conversion into alcohol at a suitable rate of passage being approximately 80 per cent. isoButyl aldehyde and Valeric aldehyde at 140–160° C. likewise give high yields of isoButyl and Amyl alcohols, together with small quantities of the Acetals.

Within recent years there has seemed some probability that the hydrogenation of Acetaldehyde (made by hydration of Acetylene) would develop into a technical process for the manufacture of synthetic Alcohol. By using dry Aldehyde and pure Hydrogen, 80 per cent. of the former can be continuously converted by Nickel into Alcohol, and the unchanged 20 per cent. easily recovered by fractionation and returned to the reaction. At temperatures above 140° C., the conversion into Alcohol is lower than 80 per cent., while at 180° C. the formation of Methane and Carbon monoxide commences,

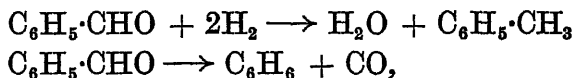


On a large scale, the Swiss Elektrizitätswerk Lonza passed Hydrogen and Acetaldehyde over finely-divided reduced Nickel, heated to 150° C., using a large excess of the former to dissipate the heat of reaction, and a trace of Oxygen (0.3 per cent.) to prevent the formation of Ether (Swiss P. 74129 of 1916; Canadian P. 134521). On a semi-large scale, the Badische Company and other works in Germany have given attention to the process, but apparently without achieving commercial success.

Reduced Cobalt reacts much less energetically than Nickel, so that the yields of Alcohol are smaller. Copper requires a higher temperature, so that the reverse change, dehydrogenation, is favoured. Platinum sponge acts slowly, and reduction is generally very incomplete.

Aromatic aldehydes do not give the corresponding Alcohol.

The :CO group is either reduced to :CH₂ or is eliminated altogether. Thus, Benzaldehyde with Nickel at 210–240° C. gives Toluene and Benzene,



which are accompanied by a certain amount of the corresponding Cyclohexane derivatives.

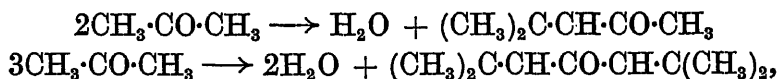
Reduction of Ketones

Aliphatic Ketones are stabler than the aldehydes towards catalytic Nickel, and can generally be reduced almost quantitatively to the corresponding secondary alcohols. Pinacones are not formed from simple ketones by catalytic methods of reduction, a considerable advantage over the common chemical methods.

Acetone, with catalytic Nickel at 115–125° C. gives isoPropyl alcohol. Methyl ethyl ketone, Diethyl ketone, Methyl propyl ketone, Ethyl isopropyl ketone, Methyl butyl ketone and Di-isopropyl ketone also, at temperatures below 150° C., give the corresponding secondary alcohols (Sabatier and Senderens, *C.R.*, 1903, 137, 301; Amouroux, *Bull. Soc. chim.*, 1910, (4), 7, 154).

Cobalt is less energetic than Nickel. Copper, by requiring a higher temperature, induces the reverse reaction, namely, dehydrogenation, while Platinum sponge is slow.

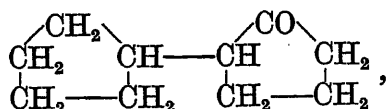
At higher temperatures than 150° C., Nickel sometimes induces a more complicated change. Thus, Haller and Lassieur (*C.R.*, 1910, 150, 1013) showed that Methyl nonyl ketone, an obnoxious constituent of coconut oil, gives on hydrogenation with Nickel at 250–300° C. a hydrocarbon, C₉H₂₀, and a Pinacone, C₉H₁₉·C(CH₃)₂·CO·C₉H₁₉. Lassieur (*ibid.*, 1913, 156, 795) also reduced Acetone in the presence of catalytic Nickel at temperatures above 200° C. isoPropyl alcohol and Pinacone were not formed in appreciable quantities, isoButyl acetone and Di-isobutyl ketone (Valerone) being the main products, with small quantities of a substance not identified. Evidently, at 200° C., in contact with Nickel, Acetone undergoes condensation to Mesityl oxide and Phorone,



and these two substances, by hydrogenation of the ethylene linkages, give respectively Methyl isobutyl ketone and Di-isobutyl ketone.

Alicyclic Ketones also are reduced by Hydrogen in presence of Nickel, generally giving more or less of the secondary alcohol, with various bye-reactions.

Cyclopentanone, hydrogenated in presence of catalytic Nickel at 125° C., gives mainly Cyclopentanol, yield 50 per cent., but a dicyclic ketone, probably α -Cyclopentyl cyclopentanone,

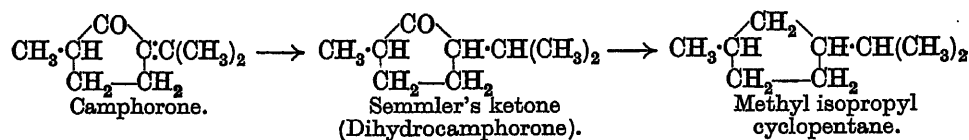


is also formed, in a yield up to 40 per cent., together with small quantities of Cyclopentane (Godchot and Taboury, *C.R.*, 1911, 152, 881).

The same investigators reduced β -Methyl cyclopentanone in presence of Nickel at 150° C. (*Bull. Soc. chim.*, 1913, 13, 591), and obtained β -Methyl cyclopentanol, but the chief product appeared to consist of mixed stereoisomers of a dicyclic ketone, probably $\beta\beta'$ -Dimethyl cyclopentyl cyclopentanone, $\text{C}_{12}\text{H}_{20}\text{O}$.

The same Methyl cyclopentanone was, however, reduced by Zelinsky (*Ber.*, 1911, 44, 2779, 2781, 2782), who stated that with Nickel at 150–160° C. the :CO group was partly reduced to :CH₂, and partly to :CHOH, so that the product was a mixture of Methyl cyclopentane and Methyl cyclopentanol, with a little unchanged ketone. At 250° C., reduction took the first course almost exclusively, and a good yield of Methyl cyclopentane was obtained.

Frequently Cyclopentane derivatives are reduced in a way resembling Acetophenone. Thus, Godchot and Taboury (*C.R.* 1913, 156, 470) found that Camphorone, with catalytic Nickel at 130° C., was reduced to Dihydrocamphorone, identical with Semmler's ketone (*Ann.*, 327, 136), and that this, in turn, at 180° C. was further reduced to the hydrocarbon 1-Methyl 3-isopropyl cyclopentane,



Cyclohexanone and its three isomeric Methyl derivatives are easily reduced in contact with Nickel at 180° C. to the corresponding Cyclohexanols, with small quantities of the Cyclohexanes (Sabatier and Senderens, *Ann. Chim. Phys.*, 1905, (8), 4, 402).

"Pulegomenthone," $(\text{CH}_3)_2\text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_3$, gives a mixture of Menthol and "Pulegomenthol" when reduced in contact with Nickel at 140–160° C. (Haller and Martine, *C.R.*, 1905, 140, 1298).

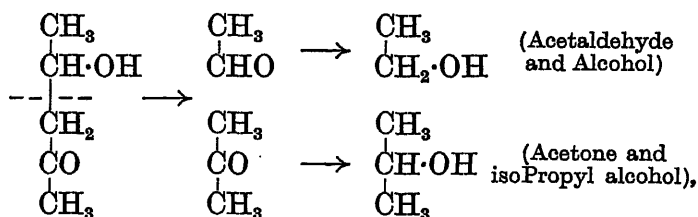
Zelinsky carried out hydrogenations of cyclic ketones at low

pressures, but found no marked difference in the course of reaction. Hydrogen, saturated with the vapour of 1:3-Dimethyl 3-cyclohexene-5-one at 150° C., was led over catalytic Nickel at 200° C., at a pressure of 70–80 mm. The products were 1:3-Dimethyl 5-cyclohexanone and 1:3-Dimethyl cyclohexanol.

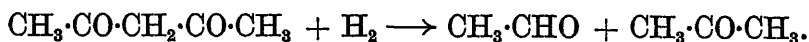
Diketones were found by Sabatier and Mailhe (*C.R.*, 1907, 144, 1086) to be easily reduced, and to react differently according to the relative positions of the two ketonic groups.

Diacetyl, $\text{CH}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_3$, an α -diketone, when passed with Hydrogen over Nickel at 140–150° C., is reduced to a mixture of approximately equal parts of Dimethyl ketol, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot\text{OH}\cdot\text{CH}_3$, and Dimethyl glycol, $\text{CH}_3\cdot\text{CH}\cdot\text{OH}\cdot\text{CHOH}\cdot\text{CH}_3$.

Acetyl acetone, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$, a β -diketone, with catalytic Nickel at 150° C., is first reduced to the corresponding keto-alcohol, $\text{CH}_3\cdot\text{CH}\cdot\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$, which is obtainable in a yield of about 25 per cent. of theory. The remaining 75 per cent. of the Acetyl acetone is recovered as a mixture of Acetaldehyde, Acetone, Ethyl alcohol, and isoPropyl alcohol. These are either formed from the keto alcohol by scission and reduction, thus,

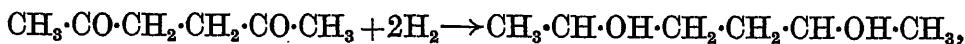


or by the original diketone reacting in a second way—



The former explanation is the more probable, since the higher the temperature the less keto alcohol is obtained and the greater the production of the simpler products. If Methyl acetyl acetone, a β -diketone of the structure $\text{CH}_3\cdot\text{CO}\cdot\text{CH}(\text{CH}_3)\cdot\text{CO}\cdot\text{CH}_3$, is used, the scission reaction and reduction take place almost exclusively, and the products are Acetaldehyde, Ethyl alcohol, Methyl ethyl ketone, and isoButyl alcohol, with very little liquid corresponding with the keto alcohol.

Acetonyl acetone, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$, a γ -diketone, with Nickel at 190° C., gives almost quantitatively Hexylene oxide and water. The reaction therefore takes the "normal" course, thus:

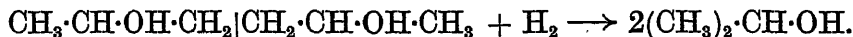


but the dihydroxy-hexane thus formed, in accord with the general

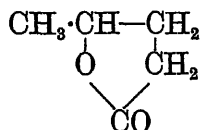
rule, produces the internal anhydride, a five-membered ring compound of the structure

$$\begin{array}{c} \text{CH}_2 \cdot \text{CH}(\text{CH}_3) \\ | \quad \quad | \\ \text{CH}_2 \cdot \text{CH}(\text{CH}_3) \end{array} \text{>O}.$$

At the same time, a very small quantity of the Dihydroxyhexane is hydrogenated to isoPropyl alcohol, thus,

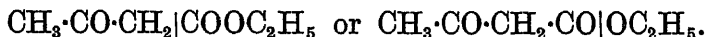


Keto Acids and Esters. These behave, in the main, like diketones in which the keto groups occupy corresponding relative positions. Thus, Levulic acid, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$, with Nickel at 250°C ., behaves like a γ -diketone, and gives Valerolactone,

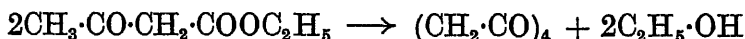


(Sabatier and Mailhe, *Ann. Chim. Phys.*, 1909, (8), 16, 78).

Acetoacetic ester, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$, behaves rather like a β -diketone, giving three simultaneous reactions: (1) Reduction of the keto-group, giving Ethyl butyrate, $\text{CH}_3 \cdot (\text{CH}_2)_2 \cdot \text{COOC}_2\text{H}_5$. (2) The molecule splits into fragments in two ways, and the fragments are independently hydrogenated, giving Acetone, isoPropyl alcohol, Ethyl alcohol, and Propionic acid, thus,



(3) A molecular condensation giving Dehydracetic acid,



(Sabatier and Mailhe, *Bull. Soc. chim.*, 1908, (4), 3, 232; *Ann. Chim. Phys.*, 1909, (8), 16, 70).

Mixed Aliphatic-Aromatic Ketones are generally reduced by Nickel to hydrocarbons containing an equal number of Carbon atoms, the :CO group becoming :CH_2 . With Nickel of only moderate catalytic activity prepared by reduction of the oxide above 300°C ., good yields of hydrocarbon result, while highly active Nickel, prepared at a low temperature, causes hydrogenation of the aromatic nucleus at the same time.

In presence of Nickel of moderate activity (reduced above 300°C .), at 190 – 195°C ., Darzens prepared the following hydrocarbons (*C.R.*, 1904, 139, 868): Ethyl benzene from Acetophenone, para-Methyl ethyl benzene from para-Tolyl methyl ketone, para-Ethyl tertiary butyl benzene from para-Butyl acetophenone, Butyl benzene from Benzyl acetone. Using actively catalytic Nickel, the aromatic

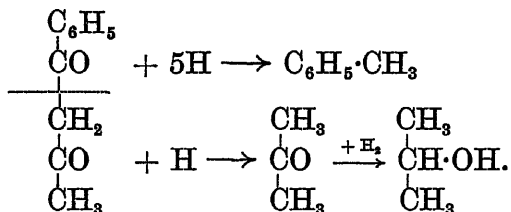
nucleus was also hydrogenated. Using active Nickel at 175° C., Sabatier and Murat prepared Dicyclohexyl propane, $C_6H_{11}(CH_2)_3 \cdot C_6H_{11}$, from Dibenzyl ketone $(C_6H_5 \cdot CH_2)_2CO$ (*C.R.*, 1912, 155, 385).

Naphthyl alkyl ketones, like the phenyl analogues, are converted quantitatively into hydrocarbon by hydrogenation at 180° C. with Nickel, prepared by reduction of the oxide at 250° C. Darzens and Rost prepared α - and β -Ethyl naphthalenes from α - and β -Acetyl naphthalenes and α - and β -isoButyl naphthalenes from α - and β -isoButyryl naphthalenes (*C.R.*, 1908, 146, 933).

Godchot (*Bull. Soc. chim.*, 1907, (4), I, 710) reduced Hexahydroanthrone, $C_6H_{10} \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} C_6H_4$, to the corresponding hydrocarbon, Octahydroanthracene, $C_6H_{10} \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ CH_2 \end{smallmatrix} C_6H_4$, with Hydrogen and Nickel at 200° C.

Aromatic Diketones, like the simple ketones, are reduced by Hydrogen in presence of Nickel to hydrocarbons containing the same number of Carbon atoms (Sabatier and Mailhe, *C.R.*, 1907, 145, 426, 1126). Benzoin, $C_6H_5 \cdot CO \cdot CH \cdot OH \cdot C_6H_5$, and Benzil, $C_6H_5 \cdot CO \cdot CO \cdot C_6H_5$, with catalytic Nickel at 200–230° C., are reduced quantitatively to symmetrical Diphenyl ethane (Dibenzyl), $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$.

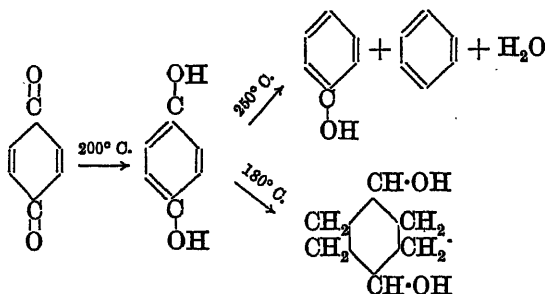
Mixed Aliphatic-Aromatic Diketones, like Benzoyl acetone, $C_6H_5 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$, behave similarly. With catalytic Nickel at 200° C., Benzoyl acetone gives an 80 per cent. yield of Butyl benzene, with small quantities of the hexahydro-derivative. The remaining 20 per cent. of the Benzoyl acetone behaves in a manner suggestive of the β -diketones, the molecule splitting into two fragments which undergo separate reduction, forming Acetone, isoPropyl alcohol and Toluene, thus :



Quinones. Sabatier and Mailhe (*C.R.*, 1908, 146, 457) showed that these behave like γ -diketones, reducing easily to the corresponding dihydroxy-bodies.

From Benzoquinone, Toluquinone, para-Xyloquinone, and Thymoquinone the corresponding para-diphenols were formed almost quantitatively by hydrogenation in presence of Nickel at 200° C. At higher temperatures, 220–250° C., the diphenols may be further

reduced, giving water, the monophenolic bodies, and the corresponding hydrocarbons. At lower temperatures than 200°C ., the diphenols may be reduced to the corresponding dihydroxy-bodies of the Cyclohexane series. Thus,

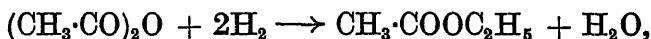


Anhydrides

When the anhydride of a fatty acid is treated with excess of Hydrogen in presence of catalytic Nickel at 180°C ., the corresponding acid and aldehyde are the first products,



This reaction is quickly followed by hydrogenation of the aldehyde to primary alcohol, which in turn is esterified by the acid, or by unchanged anhydride. The products, therefore, are (1) Fatty acid, (2) Alcohol, (3) Aldehyde, (4) Ester (Sabatier and Mailhe, *C.R.*, 1907, 145, 18). The alternative course represented by the equation



followed by partial decomposition of Ethyl acetate into Acetaldehyde and Ethyl alcohol, is less likely, since Ethyl acetate is not attacked at 180°C . Acetic anhydride therefore gives a little Acetaldehyde, Ethyl acetate, Ethyl alcohol, and Acetic acid. Propionic, Butyric, and Methyl butyric anhydrides behave similarly. The proportions of aldehyde increase and of acid diminish as the carbon content of the original anhydride increases. Copper at $200\text{--}210^{\circ}\text{C}$. reacts like Nickel at 180°C .

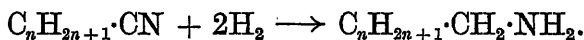
Anhydrides of dibasic acids behave in a much simpler manner, giving the lactone of an acid containing the same number of Carbon atoms. Thus, Succinic anhydride, $\begin{array}{c} \text{CH}_2-\text{CO} \\ | \quad \diagup \\ \text{CH}_2-\text{CO} \end{array} \text{O}$, gives γ -oxyButyrolactone, $\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ | \quad \diagup \\ \text{CH}_2-\text{CO} \end{array} \text{O}$, with a little Succinic acid formed by hydrolysis with the water resulting from the main reaction. Camphoric anhydride, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{O}$, gives Campholide, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{O}$,

almost quantitatively, while Citraconic acid is partially reduced to Pyrotartaric (Eijkman, *Chem. Weekblad*, 1907, 4, 191). Phthalic anhydride, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} O$, with Nickel at 200° C., similarly gives Phthalide, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} O$, quantitatively (Godchot, *Bull. Soc. chim.*, 1907, (4), I, 829).

REDUCTION OF NITROGEN COMPOUNDS

Nitriles

Aliphatic. Finely-divided reduced Nickel at 180–200° C. or finely-divided reduced Copper up to 300° C. hydrogenates aliphatic nitriles to the primary amines containing an equal number of Carbon atoms,

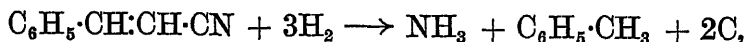


Since primary amines interact under the influence of heated catalytic metals, the reaction proceeds farther, a considerable portion being converted, with loss of Ammonia, into the corresponding secondary and tertiary amines. The final product is therefore a mixture of the three amines in which, when the reaction is carried out at about 200° C., the secondary usually preponderates (Sabatier and Senderens, *C.R.*, 1905, 140, 482; *Bull. Soc. chim.*, 1905, (3), 88, 371; Mailhe, *Chem. Zeit.*, 1905, 99, 462; 1906, 30, 458).

Hydrocyanic acid is difficult to hydrogenate and requires an unusually high temperature. At about 250° C., with Nickel it gives a mixture of Ammonia and the three Methylamines. Platinum is temporarily effective in this reaction at 120° C. Acetonitrile, $CH_3 \cdot CN$, is easily hydrogenated with Nickel at 200° C. to a mixture of the three Ethylamines, containing about 60 per cent. of Diethylamine and 20 per cent. each of Mono- and Tri-ethylamines. Propionitrile, $CH_3 \cdot CH_2 \cdot CN$, with Nickel at 200° C., is hydrogenated to a mixture of about 10 per cent. Mono-, 70 per cent. Di-, and 20 per cent. Tri-propylamines. In some cases, reduction of the amines to hydrocarbon and Ammonia is unavoidable, for example, the Hexonitrile, $(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot CN$, which is hydrogenated by Nickel at 200–220° C. to a mixture of isoHexylamine, $(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$; Di-isoHexylamine, $[(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot CH_2]_2NH$, which is the main product; Tri-isoHexylamine, $[(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot CH_2]_3N$, and β -Methyl pentane, $(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot CH_3$, formed by complete reduction accompanied by elimination of Ammonia.

In certain cases, unsaturated nitriles can be reduced to the corresponding unsaturated amines, addition of Hydrogen to the cyanogen group occurring before the ethylenic linkage is reduced. Thus,

Mailhe passed Crotononitrile, $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CN}$, with excess of Hydrogen over catalytic Nickel at $200\text{--}210^\circ\text{C}$. Much Ammonia was produced and a liquid condensed which commenced to boil at 80°C . A considerable fraction boiling at $81\text{--}85^\circ\text{C}$. proved to be Crotonylamine, $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{NH}_2$. Pursuing the distillation, unchanged nitrile passed over at 120°C ., followed by an alkaline liquid at about 130°C ., which proved to be largely Dicrotonylamine, $(\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CH}_2)_2\text{NH}$. Butylamine was not formed in sufficient quantity to be detected by fractional distillation. Oleonitrile, $\text{C}_{17}\text{H}_{33}\cdot\text{CN}$, passed with a swift current of Hydrogen over catalytic Nickel, gave much Ammonia and a small quantity of a strongly alkaline liquid corresponding with the amine, but owing to the low volatility of the nitrile the catalyst soon became inert. Cinnamonitrile, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CN}$, was similarly hydrogenated with Nickel at $250\text{--}260^\circ\text{C}$. Again a large quantity of Ammonia was evolved and the liquid which collected commenced to boil at 80°C ., rapidly rising to 180°C . The lower fractions consisted of Benzene and homologues,

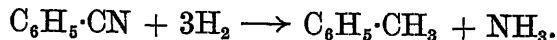


while the higher, consisting of a small quantity of an alkaline liquid boiling about 255°C ., contained the primary amine,



mixed probably with a little of the saturated amine (Mailhe, *Bull. Soc. chim.*, 1920, 27, 226).

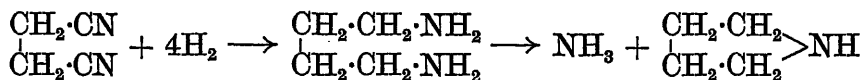
Aromatic. Sabatier and Senderens found that when aromatic nitriles are passed with Hydrogen over catalytic Nickel at 200°C ., amines are not formed, but almost exclusively the products of complete hydrogenation, namely, hydrocarbon and Ammonia. Thus, Benzonitrile gave Toluene and Ammonia,



Using Copper as catalyst, however, they succeeded in obtaining the three Benzylamines from Benzonitrile.

Frébault (*C.R.*, 1905, 140, 1036), repeating Sabatier and Senderens' work, found that by modifying the conditions the aromatic nitriles could be made to react in the same way as the aliphatic, and give a mixture of the corresponding primary and secondary amines. Maintaining a strictly uniform temperature of about 250°C . by embedding the reaction tube in iron filings, using a rapid Hydrogen stream, and allowing the nitrile to drip directly into the reaction tube, Frébault obtained from Benzonitrile, Benzylamine, and Dibenzylamine in almost equal quantities with a trace of crystalline substance, probably Tribenzylamine; and from para-Toluonitrile he obtained in the same way para-Methyl benzylamine, and Di-para-methyl benzylamine.

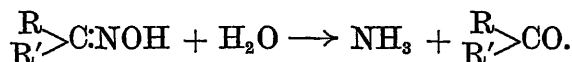
Dinitriles. Ethylene dicyanide undergoes the normal course of hydrogenation in contact with catalytic Nickel, giving Tetramethylene diamine, which is partially resolved into Pyrrolidine and Ammonia,



(Gaudion, *Bull. Soc. Chim.*, 1910, (4), 7, 824).

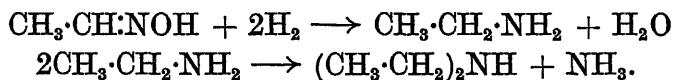
Oximes

When hydrogenated in presence of Nickel, Cobalt, Iron, or Copper oximes generally yield the corresponding primary amines, which are partially transformed into the secondary with loss of Ammonia. Traces only of tertiary amines, as a rule, are obtained. Bye-reactions are numerous, the commonest being (1) Hydrolysis of the oxime with the water formed in the reaction, whereby the corresponding aldehyde or ketone is regenerated,



(2) Reduction beyond the amine stage. This always happens if the temperature of the catalyst is too high. For instance, Nickel at 250° C. gives Ammonia and hydrocarbon, and at 300° C., still lower degradation products.

Aliphatic Aldoximes. The lower aldoximes, hydrogenated in presence of Nickel at 180–220° C., or Copper (reduced at 150–200° C.) at about 300° C. give mainly the corresponding secondary amine, and smaller quantities of the primary. For example, Acetaldoxime, $\text{CH}_3 \cdot \text{CH} \cdot \text{NOH}$, gives mainly Diethylamine and some Ethylamine,



With the oximes of the higher aliphatic aldehydes, however, the primary amine preponderates. Thus, Heptaldoxime, hydrogenated in presence of Nickel at 210–220° C., gives a mixture of the corresponding primary, secondary, and tertiary amines in the ratio of 13 : 6 : 1 (Mailhe, *C.R.*, 1905, 140, 1691; 141, 113).

Aliphatic Ketoximes. Those behave like the aldoximes and give with Nickel at 150–200° C., or with Copper at about 300° C., a mixture of the corresponding primary and secondary amines, mainly the latter, and very little of the tertiary.

Acetoxime, $(\text{CH}_3)_2\text{C} \cdot \text{NOH}$, with catalytic Nickel at 150–180° C. gives a product consisting of about 33 per cent. isoPropylamine and 66 per cent. Di-isopropylamine. A trace of triamine is probably

present. Methyl ethyl ketoxime, $\text{CH}_3\text{C}_2\text{H}_5 > \text{C:NOH}$, with Nickel at $150\text{--}200^\circ \text{C}$., or Copper at 300°C ., gives a similar mixture of about 33 per cent. secondary Butylamine and 66 per cent. di-secondary Butylamine. Methyl *n*-propyl ketoxime, $\text{CH}_3\text{C}_3\text{H}_7 > \text{C:NOH}$, with Nickel at $180\text{--}200^\circ \text{C}$., gives a mixture of 40 per cent. secondary Amylamine and 60 per cent. of di-secondary Amylamine (Mailhe, *loc. cit.*).

Cyclic Ketoximes give analogous reactions, but the primary amine is the main product.

Cyclohexanone oxime, $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{C:NOH}$, with Nickel at 190°C ., gives chiefly Cyclohexylamine and a little Dicyclohexylamine and Aniline (Amouroux, *Bull. Soc. chim.*, 1911, (4), 9, 214). The Methyl cyclohexanone oximes, however, do not react so smoothly, thus: Ortho- and meta-Methyl cyclohexanone oximes give some of the corresponding ortho- and meta-Methyl cyclohexylamines, and Di-ortho- and -meta-methyl cyclohexylamines, but mostly ortho- and meta-Methyl cyclohexanone. Para-Methyl cyclohexanone oxime gives para-Methyl cyclohexylamine and Di-para-methyl cyclohexylamine with some of the hexanone and hexene. Menthone oxime reacts easily, and gives Menthylamine, Dimenthylamine, and Menthane in the normal way (Mailhe and Murat, *Bull. Soc. chim.*, 1911, (4), 9, 464). Camphor oxime gives the corresponding primary and secondary amines in good yield (Aloy and Brustier, *Bull. Soc. chim.*, 1911, (4), 9, 734).

Aromatic Aldoximes. Using Nickel, the hydrocarbon containing the same number of Carbon atoms is generally the main product, thus: Benzaldoxime, $\text{C}_6\text{H}_5 \cdot \text{CH:NOH}$, with catalytic Nickel gives Toluene and Ammonia. If Copper at $220\text{--}230^\circ \text{C}$ is used, Benzaldehyde is the main product, but Benzylamine, Dibenzylamine, and Tribenzylamine are also formed. These are regarded as secondary products, the oxime first producing Benzaldehyde, Benzonitrile, and water, the three amines then being formed by hydrogenation of the nitrile.

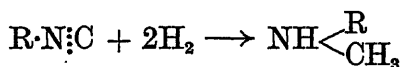
Aromatic Ketoximes behave like the aliphatic, but since they are more difficult to vaporise, and frequently less stable, the yields of amine are poorer. To minimise decomposition, it is necessary to work at the lowest possible temperature and to use a fast current of Hydrogen. Acetophenone oxime, $\text{C}_6\text{H}_5\text{CH}_3 > \text{C:NOH}$, with Nickel at $250\text{--}270^\circ \text{C}$., gives $\text{C}_6\text{H}_5\text{CH}_3 > \text{CH} \cdot \text{NH}_2$ and $(\text{C}_6\text{H}_5\text{CH}_3 > \text{CH})_2\text{NH}$, and a 20 per cent. yield of Ethyl benzene. As the aliphatic portion of the oxime becomes more complex the reaction becomes less satisfactory,

thus, under the same conditions Propiophenone oxime, $\text{C}_6\text{H}_5\text{C}(\text{C}_2\text{H}_5)_2\text{C}:\text{NOH}$, gives 70 per cent. of a mixture of Propyl benzene, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$, and Propenyl benzene, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CH}_3$, with a little $\text{C}_6\text{H}_5\text{C}(\text{C}_2\text{H}_5)_2\text{CH}\cdot\text{NH}_2$ and 15 per cent. of $(\text{C}_6\text{H}_5\text{C}(\text{C}_2\text{H}_5)_2\text{CH})_2\text{NH}$. Butyrophenone oxime, $\text{C}_6\text{H}_5\text{C}(\text{C}_3\text{H}_7)_2\text{C}:\text{NOH}$, gives a little $\text{C}_6\text{H}_5\text{C}(\text{C}_3\text{H}_7)_2\text{CH}\cdot\text{NH}_2$ and $(\text{C}_6\text{H}_5\text{C}(\text{C}_3\text{H}_7)_2\text{CH})_2\text{NH}$, and much $\text{C}_6\text{H}_5\cdot\text{C}_4\text{H}_9$ and $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{C}_2\text{H}_5$.

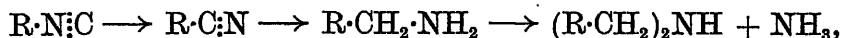
Benzophenone oxime, $(\text{C}_6\text{H}_5)_2\text{C}:\text{NOH}$, on the other hand, gives a 70 per cent. yield of the corresponding primary amine, $(\text{C}_6\text{H}_5)_2\text{CH}\cdot\text{NH}_2$, and a little of the secondary amine, $(\text{C}_6\text{H}_5)_2\text{CH}\text{CH}(\text{C}_6\text{H}_5)_2\text{NH}$ (Mailhe and Murat, *Bull. Soc. chim.*, 1911, IV, 9, 464).

Carbylamines or Isocyanides

Aliphatic carbylamines are reduced by catalytic Nickel at 160–180° C. mainly to the corresponding secondary amines,

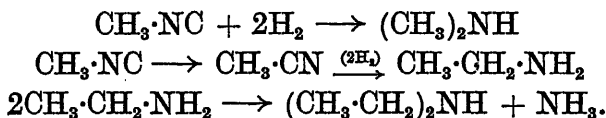


(Sabatier and Mailhe, *C.R.*, 1907, 144, 955). A certain portion of the isocyanide is, however, isomerised to cyanide or nitrile, which is then reduced, giving ammonia and primary and secondary amines,



while a third portion is polymerised, with formation of tar, which is deposited on the Nickel and soon impedes its catalytic action. At higher temperatures, 220–250° C., the secondary amine undergoes further hydrogenation, yielding hydrocarbons and Ammonia. This is specially noticeable with the more complex carbylamines.

Hydrogen impregnated with the vapour of Methyl carbylamine, $\text{CH}_3\cdot\text{NC}$, and passed over Nickel at 160–180° C., gives an 80 per cent. yield of Dimethylamine. At the same time, isomerisation and reduction lead to formation of Ethylamine and Diethylamine,

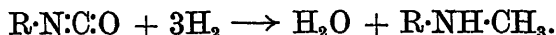


Similarly, Ethyl carbylamine, $\text{C}_2\text{H}_5\cdot\text{NC}$, gives mainly Methyl ethyl amine, with a little Propylamine and Dipropylamine, and tertiary Butyl carbylamine, $(\text{CH}_3)_3\text{C}\cdot\text{NC}$, gives Methyl tertiary butyl amine,

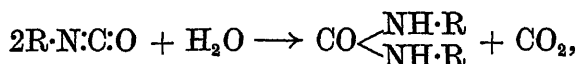
$\text{CH}_3\cdot\text{NH}\cdot\text{C}(\text{CH}_3)_3$, with small quantities of Dimethyl propylamine and higher boiling secondary amines. Copper also brings about hydrogenation of Carbylamines, but its action is less rapid (Sabatier and Mailhe, *Ann. Chim. Phys.*, 1909, (8), 16, 95).

Carbimides or Isoeyanates

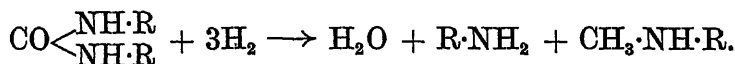
Sabatier and Mailhe (*C.R.*, 1907, 144, 824) found that when carbimides are hydrogenated in presence of Nickel at 180–190° C. the principal action leads to formation of a secondary amine, thus,



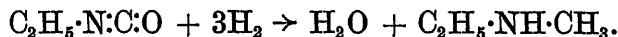
Secondary products are, however, formed, due to the water produced in this reaction acting upon the carbimide to give the corresponding carbamide, or symmetrical dialkyl urea,



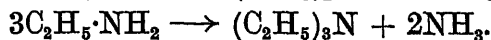
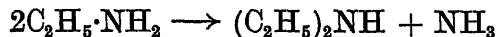
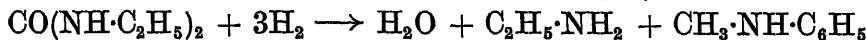
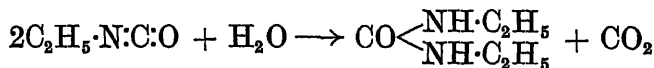
which then is hydrogenated as follows :



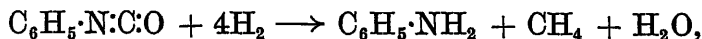
When Hydrogen impregnated with the vapour of Ethyl carbimide is passed over catalytic Nickel at 180–190° C., the chief product is Methyl ethylamine,



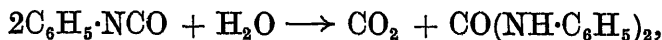
At the same time, small quantities of mono-, di-, and tri-Ethylamines are formed, together with Ammonia and Carbon dioxide, but no Methane, as follows :



Phenyl carbimide under the same conditions gives water and Aniline, Methane and Carbon dioxide. At the same time, on examining the catalyst it is found that the Nickel has become thickly encrusted with Diphenyl carbimide. The principal reaction is therefore



the water so formed then reacting with unchanged Phenyl carbimide,

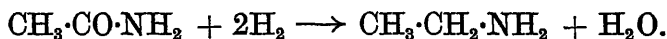


to give the non-volatile Diphenyl carbamide, which is deposited in the catalyst.

Amides

Aliphatic acid amides (except Formamide) are hydrogenated in contact with Nickel at 200–230° C., or Copper at 200–300° C., to the corresponding primary and secondary amines (Mailhe, *Bull. Soc. chim.*, 1906, (3), 35, 614; *Chem. Zeit.*, 1906, 30, 458).

Acetamide, $\text{CH}_3\cdot\text{CO}\cdot\text{NH}_2$, with Nickel at 230° C., is hydrogenated to Ethylamine and Diethylamine,

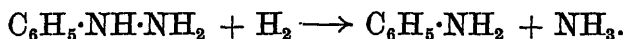


Propionamide similarly gives Propylamine and Dipropylamine.

Azo- and Hydrazo-compounds

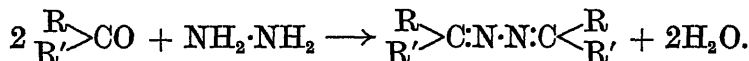
Azobenzene, $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_5$, sublimed with Hydrogen over catalytic Nickel, readily gives Aniline (Sabatier and Senderens, *Bull. Soc. chim.*, 1906, (3), 35, 259).

Phenyl Hydrazine, hydrogenated with Nickel at 210° C., first splits into Aniline and Ammonia,

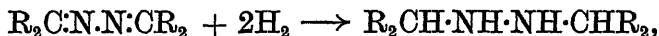


The Aniline is then partially hydrogenated to Cyclohexylamine and Dicyclohexylamine, while a little is decomposed into Benzene and Cyclohexane (Sabatier and Senderens, *Bull. Soc. chim.*, 1906, (3), 35, 259).

Azines. Aldehydes and ketones readily condense with Hydrazine when 2 molecules of the former are mixed with 1 molecule of the latter in the form either of Hydrazine hydrate or a basified Hydrazine salt. Generally the reaction is vigorous and must be modified by the presence of a solvent. The reactants in the correct proportion are dissolved in suitable solvents (usually water or Alcohol), mixed, and the resulting solution either heated or cooled, according to the ease with which interaction occurs. The azine can then be isolated by evaporating excess of the solvent, and allowing to crystallise,



Mailhe expected to obtain symmetrical hydrazines by regulated low temperature hydrogenation of azines,



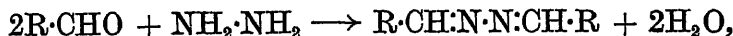
but in no case was this expectation realised, either with aldazines

or ketazines. The first product which could be isolated was always the corresponding primary amine,

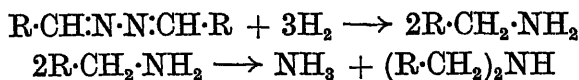


which tended in the usual way to lose Ammonia, with formation of the secondary, and sometimes also of the tertiary, amine.

Aldazines prepared by condensation between aldehydes and Hydrazine,



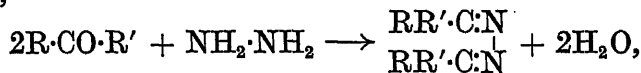
when sublimed with excess of Hydrogen over Nickel at 140–160° C., are reduced to a mixture of primary, secondary, and tertiary amines, the relative proportions varying with the temperature of the catalyst and the azine used,



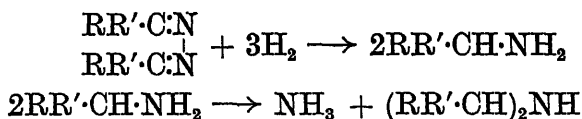
(Mailhe, *C.R.*, 1920, 170, 1120; *Bull. Soc. chim.*, 1920, 27, 541).

Diethylidene or Acetaldehyde azine, $CH_3 \cdot CH:N:N:CH \cdot CH_3$, passed with Hydrogen over Nickel at 140–150° C., gives Ethylamine, with larger amounts of di- and tri-Ethylamines. Di-isobutylidene azine, $(CH_3)_2CH \cdot CH:N:N:CH \cdot CH(CH_3)_2$, with Nickel at 160° C., gives isoButylamine, Di-isobutylamine, a little Tri-isobutylamine, and Ammonia. Di-isoamylidene or isoValeric aldehyde azine, $(CH_3)_2CH \cdot CH_2 \cdot CH:N:N:CH \cdot CH_2 \cdot CH \cdot CH(CH_3)_2$, with Nickel at 180° C., gives mainly isoAmylamine, with small quantities of the secondary and tertiary amines. At 210–230° C., however, twice as much secondary as primary amine is formed, but still small quantities only of tertiary.

Ketazines prepared by condensation between ketones and Hydrazine,



undergo a similar reaction when sublimed with Hydrogen over catalytic Nickel at 150–200° C., yielding primary and secondary amines, the former predominating at lower temperatures of hydrogenation, the latter at higher,



(Mailhe, *C.R.*, 1920, 170, 1265).

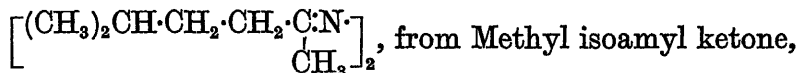
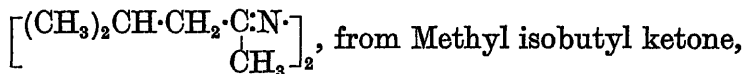
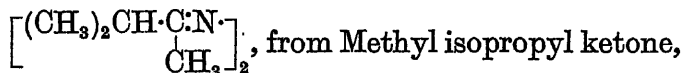
Dimethyl ketazine, $(\text{CH}_3)_2\text{C}:\text{N}:\text{N}:\text{C}(\text{CH}_3)_2$, from Acetone and Hydrazine, gives at 150°C ., a mixture of isoPropylamine, $(\text{CH}_3)_2\text{CH}\cdot\text{NH}_2$, and Di-isopropylamine, the latter in larger amount. Diethyl ketazine, $(\text{C}_2\text{H}_5)_2\text{C}:\text{N}:\text{N}:\text{C}(\text{C}_2\text{H}_5)_2$, from Diethyl ketone, with Nickel at $160\text{--}170^\circ\text{C}$., gives chiefly 3-Amino pentane, $(\text{C}_2\text{H}_5)_2\text{CH}\cdot\text{NH}_2$, and a little secondary amine. Di-isopropyl ketazine, from Butyrone,



with Nickel at 170°C ., gives mainly the primary amine, $[(\text{CH}_3)_2\text{CH}]_2\text{CH}\cdot\text{NH}_2$, with small quantities of the secondary. Dipropyl ketazine, from Dipropyl ketone, $(\text{C}_3\text{H}_7)_2\text{C}:\text{N}:\text{N}:\text{C}(\text{C}_3\text{H}_7)_2$, hydrogenated at 170°C . in the same way, gives principally the primary amine, $(\text{C}_3\text{H}_7)_2\text{CH}\cdot\text{NH}_2$, while Di-isobutyl ketazine from iso-Valerone, with Nickel at $215\text{--}220^\circ\text{C}$., gives Ammonia and a mixture of the primary and secondary amines, $\frac{(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2}{(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2}>\text{CH}\cdot\text{NH}_2$ and $\left[\frac{(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2}{(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2}>\text{CH}\right]_2\text{NH}$, the latter predominating in the ratio of 2 : 7.

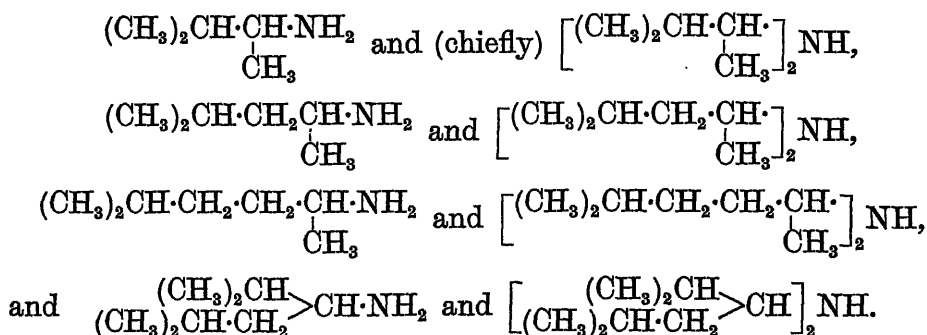
The method has recently been extended to reduction of azines from unsymmetrical ketones (Mailhe, *C.R.*, 1921, 172, 692; *Bull. Soc. chim.*, 1921, IV, 29, 219), with results as follows. Methyl propyl ketone, $\text{CH}_3\text{COC}_3\text{H}_7$, gives the azine, $\frac{\text{C}_3\text{H}_7}{\text{CH}_3}>\text{C}:\text{N}:\text{N}:\text{C}<\frac{\text{C}_3\text{H}_7}{\text{CH}_3}$, which hydrogenates to Ammonia, and a mixture of the corresponding primary and secondary amines, β -Aminopentane, $\frac{\text{C}_3\text{H}_7}{\text{CH}_3}>\text{CH}\cdot\text{NH}_2$ and $\left(\frac{\text{C}_3\text{H}_7}{\text{CH}_3}>\text{CH}\right)_2\text{NH}$.

In the same way, the following ketazines :



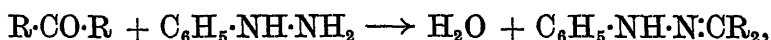
and $\left[\frac{(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2}{(\text{CH}_3)_2\text{CH}}>\text{C}:\text{N}\cdot\right]_2$, from isoPropyl isobutyl ketone give,

in addition to Ammonia, the corresponding primary and secondary amines, as follows :



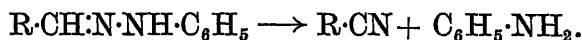
The relative proportion of primary amine increases with the complexity of the original ketone.

Phenyl Hydrazones. Aldehydes and ketones readily condense with a single molecular equivalent of substituted hydrazines, giving hydrazones,



which undergo hydrogenation in a way resembling the azines. Thus, when Phenyl hydrazones are sublimed in a rapid current of Hydrogen over catalytic Nickel at 180–190° C., reaction occurs with the formation of Aniline and other products, depending upon the type of hydrazone used (Mailhe, *C.R.*, 1921, 172, 1107; *Bull. Soc. chim.*, 1921, 29, 417).

Aldehyde Hydrazones yield Aniline and a nitrile by decomposition, with accessory formation of small quantities of amine by hydrogenation of the nitrile,



Valeric aldehyde hydrazone, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, gives chiefly Aniline and isoValeronitrile, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CN}$, with small amounts of the primary and secondary isoAmylamines,



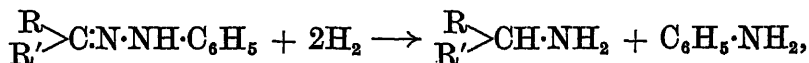
and $[(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2]_2\text{NH}$. isoButylaldehyde hydrazone,



in the same way, gives chiefly Aniline and isoButyronitrile, $(\text{CH}_3)_2\text{CH}\cdot\text{CN}$, and traces of the primary and secondary isoButylamines, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{NH}_2$ and $[(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2]_2\text{NH}$.

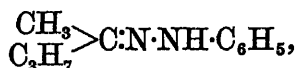
Ketone Hydrazones which are unable to yield a nitrile undergo

complete hydrogenation, without any intermediate stage, the products being Aniline and a primary amine,



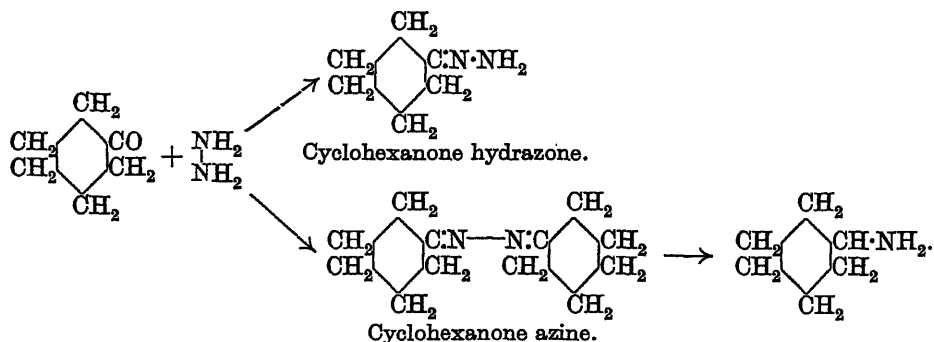
which by partial decomposition gives some secondary amine.

Acetone hydrazone, $(CH_3)_2C:N \cdot NH \cdot C_6H_5$, at $220-230^\circ C.$, gives Aniline, isoPropylamine, $(CH_3)_2CH \cdot NH_2$, and Di-isopropylamine, $[(CH_3)_2CH]_2NH$. Methyl propyl ketone hydrazone,



in the same way, gives Aniline, β -Aminopentane, $CH_3 \cdot CH_2 \cdot CH_2 \cdot \underset{NH_2}{\underset{|}{CH}} \cdot CH_3$, and some of the corresponding secondary amine.

Cyclohexanone, and its derivatives, when refluxed with Hydrazine hydrate, give mixtures of the corresponding hydrazones and azines, and hydrogenation of mixtures made in this way is one of the most satisfactory methods of obtaining Cyclohexylamine and its homologues (Mailhe, *C.R.*, 1922, 174, 465; *Bull. Soc. chim.*, 1922, 31, 340):



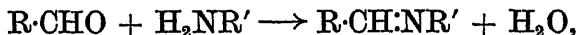
When the azine or hydrazone of Cyclohexanone, or a mixture, is volatilised with Hydrogen over catalytic Nickel at $180^\circ C.$, an excellent yield of the primary amine, Cyclohexylamine, results. The homologues of Cyclohexanone likewise give good yields of the corresponding primary amine, the formation of the secondary being comparatively small. Thus, Cyclohexanone gives Cyclohexylamine and Dicyclohexylamine in the proportions of 3 to 1. ortho-Methyl cyclohexanone gives ortho-Methyl cyclohexylamine and Di-ortho-methyl cyclohexylamine in proportions of 10 to 1. meta-Methyl cyclohexanone, which gives only the hydrazone with Hydrazine, gives almost exclusively the primary amine when the hydrazone is hydrogenated. para-Methyl cyclohexanone gives a mixture of hydrazone and ketazine which on hydrogenation produces a mixture

of para-Methyl cyclohexylamine principally, and Di-para-methyl cyclohexylamine, easily separated.

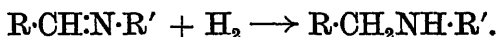
From 1:3-Dimethyl 4-cyclohexanone hydrazone, Carvone ketazine, and Menthone hydrazone, a similar good production of the corresponding primary amines was obtained (Mailhe, *Bull. Soc. chim.*, 1923, 33, 83).

Schiff's Bases

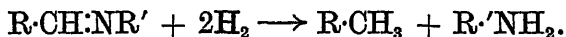
Aldehydes and primary amines very readily condense,



forming products described as Schiff's bases. These substances, when volatilised with Hydrogen over catalytic Nickel at 200–230° C., are easily reduced to the corresponding secondary amines,



At the same time, a secondary action, due to further hydrogenation, occurs, but usually only to a small extent,

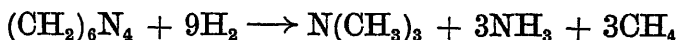


Mailhe found that the Schiff's bases made as indicated in the left-hand column of the following table were converted by hydrogenation into the substances represented in the right-hand column, the secondary amines preponderating in all cases (*Bull. Soc. chim.*, 1919, IV, 25, 321).

| Reactants. | Products. |
|--|---|
| Benzaldehyde } $\longrightarrow C_6H_5 \cdot CH:N \cdot C_6H_5$ Aniline. | $C_6H_5 \cdot \overset{C_6H_5}{CH_2} > NH$; $C_6H_5 \cdot CH_3$; $C_6H_5 \cdot NH_2$ |
| Benzaldehyde } $\longrightarrow C_6H_5 \cdot CH:N \cdot C_2H_5$ Ethylamine. | $C_6H_5 \cdot \overset{C_2H_5}{CH_2} > NH$; $C_6H_5 \cdot CH_3$; $C_2H_5 \cdot NH_2$ |
| Benzaldehyde } $\longrightarrow C_6H_5 \cdot CH:N \cdot C_6H_4 \cdot CH_3$ o-Toluidine. (1) (2) | $C_6H_5 \cdot \overset{C_6H_4 \cdot CH_3}{CH_2} > NH$; $C_6H_5 \cdot CH_3$; $C_6H_4 \cdot \begin{matrix} NH_2 (1) \\ CH_3 (2) \end{matrix}$ |
| isoValeric } $\longrightarrow C_4H_9 \cdot CH:N \cdot C_6H_5$ aldehyde Aniline. | $(CH_3)_2CH \cdot CH_2 \cdot \overset{C_6H_5}{CH_2} > NH$; C_5H_{12} ; $C_6H_5 \cdot NH_2$ |
| isoValeric } $\longrightarrow C_4H_9 \cdot CH:N \cdot C_6H_4 \cdot CH_3$ aldehyde o-Toluidine. (1) (2) | $CH_3 \cdot \overset{C_6H_4 \cdot CH_3}{CH_2} > NH$; C_5H_{12} ; $C_6H_4 \cdot \begin{matrix} CH_3 (1) \\ NH_2 (2) \end{matrix}$ |
| isoValeric } $\longrightarrow C_4H_9 \cdot CH:N \cdot C_2H_5$ aldehyde Ethylamine. | $C_4H_9 \cdot \overset{C_2H_5}{CH_2} > NH$; C_5H_{12} ; $C_2H_5 \cdot NH_2$ |

More recently, by hydrogenation of Schiff's base in liquid media, Mailhe has developed a general mode of preparation of secondary amines whereby almost quantitative yields are obtained.

Hexamethylene Tetramine. The condensation product, $(\text{CH}_2)_6\text{N}_4$, formed between Formaldehyde and Ammonia was shown by Grassi to be split completely into Trimethylamine, Ammonia, and Methane when passed with excess of Hydrogen over heated catalytic Nickel,

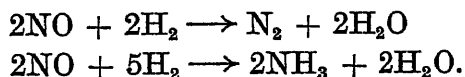


(*Gazz.*, 1906, 36, (2), 505).

Reduction of Oxides of Nitrogen

Sabatier and Senderens (*C.R.*, 1902, 135, 278) found that when Nitrous oxide, N_2O , is led with excess of Hydrogen over catalytic Nickel, reaction is rapid even at the ordinary temperature, and much heat is developed. Nitrogen and water are the products, and no Ammonia is formed. If the Nitrous oxide is in excess, the front part of the catalyst quickly becomes incandescent, and higher oxides of nitrogen appear in the cooler parts of the tube. A little Ammonia is formed.

Nitric oxide, NO , with excess of Hydrogen is not reduced by Nickel below 180°C ., but above this temperature water, Nitrogen, and Ammonia are formed. Using excess of Nitric oxide, the catalyst soon becomes incandescent,



With Nitrogen peroxide and excess of Hydrogen, the products again are Nitrogen, Ammonia, and water. If the proportion of Nitrogen peroxide is increased, Ammonium nitrite and Ammonium nitrate are formed in addition to the other three products. When the proportion of Nitrogen peroxide is high, the metal becomes incandescent, and with Nitrogen peroxide in sufficient concentration a violent explosion results.

Nitric acid vapour, with Hydrogen, over catalytic Nickel at 200°C ., gives Ammonium nitrate, while at 350°C . water, Ammonia, and Nitrogen are obtained. Copper in all the above reactions functions in the same way as Nickel, but requires a higher temperature.

Reduction of Nitro-compounds

Nitro-compounds are easily reduced when the vapour mixed with excess of Hydrogen is led over a heated catalytic metal (Sabatier and Senderens, *C.R.*, 1901, 133, 321; 1902, 135, 225; F.P. 312615 of 1901). Commonly the reaction proceeds too far. Thus, using Nickel as catalyst, various bye-reactions may take place: (1) With aromatic nitro-compounds, hydrogenation of the benzene ring. (2) The primary amine first formed in contact with the catalytic

metal decomposing into Ammonia and secondary and tertiary amines. (3) At high temperatures the catalytic metal hydrogenating beyond the amine stage, hydrocarbon and Ammonia resulting. The higher the temperature the more important this reaction becomes. Using the weakest of the catalytic metals mentioned, namely, Copper, the conditions can be adjusted so that these bye-reactions are almost entirely avoided. For reduction of nitro-compounds, water gas, or even coal gas, can be used so long as Sulphur compounds are first eliminated by contact with heated Copper.

Catalytic Nickel at 150–180° C. reduces Nitromethane exclusively to Methylamine. At higher temperatures Ammonia and Di- and Tri-methylamines are also formed. Above 250° C., and rapidly at 300° C., the reduction proceeds to Methane, Ammonia, and water. Using reduced Copper, no reaction occurs with Nitromethane and Hydrogen until a temperature of 300° C. is reached, when part of the Nitromethane is reduced, and a compound of Methylamine and Nitromethane (this presumably acting as a "pseudo"-acid) results, identical with a solution of Nitromethane in aqueous Methylamine. Nitroethane reacts in the same way. Nickel at 200° C. gives mainly Ethylamine, with small quantities of Ammonia and Di- and Tri-ethylamines. Copper reacts above 300° C. exactly as in the case of Nitromethane, forming the Ethylamine salt of the Nitroethane pseudo acid.

Nitrobenzene at 200° C. is rapidly reduced with Hydrogen in contact with catalytic Nickel. At the same time, hydrogenation of the Benzene ring occurs, and some Cyclohexylamine is formed. This bye-reaction is diminished if the Nickel is prepared by reduction of the oxide at temperatures above 300° C., and suppressed altogether if Copper at 300–400° C. is used instead. So long as excess of Hydrogen is present, the Nitrobenzene is completely reduced and no bye-products such as Azobenzene are formed (Sabatier and Senderens, *C.R.*, 1901, 133, 321). With Nickel at 250° C., Benzene, Cyclohexane, Aniline, and Ammonia are produced, while at 300° C. Benzene and Ammonia are the main products. If Hydrogen is present in large excess, much Methane is formed at 300° C., while with only a little Hydrogen, Aniline, Benzene, Ammonia, and Diphenylamine are obtained.

Reduced Cobalt and Iron (reduced from its oxide at 450–480° C.) behave like Nickel. Platinum-black reacts mildly, and small quantities of Hydrazobenzene may be isolated.

The Nitrotoluenes are reduced in the same way as Nitrobenzene. α -Nitronaphthalene, with excess of Hydrogen, and in contact with catalytic Copper at 330–350° C., gives exclusively α -Naphthylamine. If Nickel is the catalyst, reaction generally proceeds farther, with formation of more or less Tetrahydronaphthalene.

Dinitro-bodies and Nitrophenols are reduced with equal ease using a Nickel catalyst, but not with Copper. Between 170° and 210° C., the Dinitrobenzenes and Dinitrotoluenes give the corresponding diamines. Above 210° C., the diamines commence to lose Ammonia, and yield Aniline or Toluidine. Nitrophenols similarly, with Nickel at 160 – 190° C., give Amidophenols, but there is simultaneous production of Ammonia, Phenol, and Aniline. Chloronitrobenzenes in contact with Copper at 360 – 380° C., but not with Nickel, are reduced to Chloroanilines. Bromonitrobenzenes do not react so smoothly.

Nitrous Esters. From the observation of Debus, that Ethyl nitrite is reduced by Hydrogen in presence of Platinum-black to alcohol and Ammonia, it has been supposed that nitrous esters generally, on catalytic reduction, will yield Ammonia and the corresponding alcohol. This was shown by Gaudion not to be the case (*Ann. Chim. Phys.*, 1912, VIII, 25, 125).

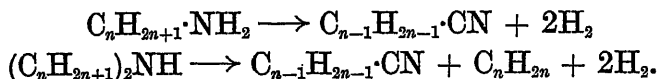
When alkyl esters of Nitrous acid are passed with Hydrogen over catalytic Nickel or Copper at a higher temperature, products are obtained similar to those obtained from the isomeric nitro-bodies. Gaudion supposed that the first change is an isomerisation of the nitrous ester to the nitro-body, which is then reduced in the usual way to a mixture of amines and Ammonia. These secondary amine was always the main product. The following nitrites were reduced: $\text{C}_2\text{H}_5\cdot\text{NO}_2$; $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{NO}_2$; $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NO}_2$, and $(\text{CH}_3)_2\text{CH}\cdot\text{NO}_2$. In the case of isoAmyl nitrite, 100 grams produced with Nickel at 220 – 230° C., 22 grams of primary, 43 grams of secondary, and 4.8 grams of tertiary isoAmylamines, and with Copper at 350° C., 29.3 grams of primary, 40.2 grams of secondary, and 2.5 grams of tertiary isoAmylamines.

The isomeric conversion of nitrous esters into nitro-compounds postulated by Gaudion has been realised experimentally by Neogi (*J.C.S.*, 1914, 105, 2371) and by Neogi and Chowdhuri (*J.C.S.*, 1916, 109, 701). The vapour of the aliphatic nitrite, diluted with paraffin, was passed through a tube packed with glass wool and heated to a suitable temperature. In the case of Methyl, Ethyl, Propyl, iso-Propyl, isoButyl and isoAmyl nitrites, the isomerisation commenced at about 100° C., and proceeded with the maximum velocity at 120 – 130° C., though still very incompletely under the experimental conditions employed. At higher temperatures, hydrolysis and oxidation of the nitrite led to formation of aldehydes and acids, this change, as well as the isomerisation, being much facilitated by the presence of water.

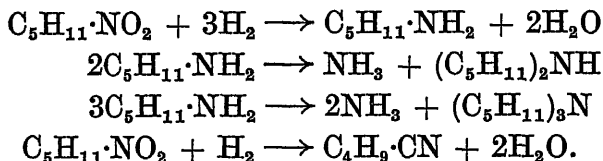
In a later research, Neogi and Chowdhuri investigated the reduction of aliphatic nitrites to amines by the method of Gaudion, using, however, a much lower temperature (*J.C.S.*, 1917, 111, 899).

They found that, using nickelised asbestos, hydrogenation of Methyl, Ethyl, Propyl, isoButyl, and isoAmyl nitrites was possible at as low a temperature as 100–130° C. when only the corresponding primary amines were formed. Iron was much less satisfactory.

The reduction of nitrous esters to amines, as carried out by Gaudion, has been extended to the preparation of nitriles. Thus, Sabatier and, independently, Mailhe, showed that when amines are passed over catalytic Nickel at a dehydrogenating temperature, loss of Hydrogen leads to the formation of nitriles,



Mailhe and Bellegarde showed that the two reactions can be carried out together; that when nitrous esters or nitro-compounds are passed with Hydrogen over Nickel at a moderately high temperature, reduction of the NO_2 group occurs, but that the process stays at the nitrile stage owing to the counter influence of dehydrogenation. Thus, when the vapour of isoAmyl nitrite is passed with Hydrogen over Nickel at 280° C., primary, secondary, and tertiary isoAmyl-amines result, together with a little isoValeronitrile,



By raising the temperature to 300–320° C., the yield of nitrile is much increased at the expense of the amines, and becomes the chief product. At the same time, a small quantity of alcohol is formed by the hydrolysis of the nitrile, a portion of which then suffers dehydrogenation, giving the corresponding aldehyde.

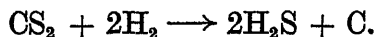
In the same way, Nitromethane gives some Hydrocyanic acid, Nitropropane gives Propionitrile, Nitro isopentane gives isoValeronitrile, and the Propyl, isoButyl, isoAmyl, and Heptyl esters of Nitrous acid give, respectively, Propionitrile, isoButyronitrile, isoValeronitrile, and Heptonitrile, together with the appropriate bye-products (*Bull. Soc. chim.*, 1919, 25, 588).

Hydrogenation of Carbon Disulphide

When the vapour of Carbon disulphide is passed with Hydrogen over reduced Nickel at 180° C., a volatile substance is formed possessing an extremely disagreeable odour. This compound forms a yellow Mercury salt, brown salts of Lead and Copper, and a white Cadmium salt, and its properties correspond with the hitherto unknown di-

mercaptan, Methylene dithiol, $\text{CH}_2(\text{SH})_2$ (Sabatier and Espil, *Bull. Soc. chim.*, 1914, (4), 15, 228).

At a higher temperature, Carbon disulphide is reduced by Hydrogen to Sulphuretted hydrogen and Carbon,



This reaction is induced by all the catalytic metals at temperatures between 440°C . and 500°C ., and is utilised on the large scale for removing the small quantities of Carbon disulphide (up to 0.02 per cent.) which always occur in crude coal gas. Purification plant at the Greenwich gas works, with a capacity of 500,000 cubic metres per day, is described by Carpenter (*J. Gas Lighting*, 1914, 126, 928; see also Evans, *J. Soc. Chem. Ind.*, 1915, 34, 9).

After removing the Sulphuretted hydrogen from the crude coal gas by appropriate absorbents, the gas is heated to 400°C . and passed over Nickel mounted upon infusorial earth, heated to $400\text{--}500^\circ \text{C}$., and contained in steel tubes 7 cm. internal diameter. Reduction of the Carbon disulphide takes place, with formation of Sulphuretted hydrogen and carbonisation and sulphurisation of the catalyst, which consequently needs frequent revivification. This is effected by passing air, which burns the Carbon and Sulphur, and forms Nickel oxide, which is reduced back to active Nickel by the first portion of coal gas that is then passed over it. After extracting the Sulphuretted hydrogen formed, the coal gas can be immediately sent to the holders.

CHAPTER VIII

DEVELOPMENT OF PROCESSES OF HYDROGENATION FROM THE TIME OF SABATIER AND SENDERENS

Introduction. Ipatiev's Researches: (a) Apparatus. Reduction of: (b) Ethylenic Compounds, (c) Aldehydes and Ketones, (d) The Aromatic Nucleus, (e) Polynuclear Hydrocarbons, (f) Terpenes. Colloidal Metals. Preparation. Use as Catalysts. Reduction of: (a) Nitrogen Compounds, (b) Ethylenic and Acetylenic Compounds, (c) Aldehydes and Ketones, (d) Aromatic Substances, (e) Nitriles and Oximes, (f) Inorganic Reactions. Willstätter's Researches. Preparation of Platinum and Palladium-black. Action of Oxygen in Hydrogenations: (a) Easy Hydrogenations, (b) Aldehydes and Ketones, (c) More Difficult Hydrogenations, (d) Fluorine Derivatives, (e) Difficult Hydrogenations, (f) Inorganic Reductions. Brochet's Researches. Preparation of Nickel Catalyst. Reduction of: (a) Unsaturated Substances, (b) Aldehydes and Ketones, (c) Dyestuffs to Leuco-bases, (d) Nitro-bodies, (e) Aromatic Compounds, (f) Nitriles, (g) Schiff's Bases. Schroeter's Researches. Purification of Naphthalene and its Hydrogenation. Tetrahydronaphthalene Derivatives. Fractional Hydrogenation. Von Braun's Researches. Hydrogenation of Indene, Acenaphthene, Quinoline, Indole, Aldehydes, Ketones, Nitriles. Hydrogenation of Oils. Historical. Catalysts: (a) Nickel, (b) Palladium and Platinum.

THE reaction of Sabatier and Senderens provided a means whereby all volatile substances not containing a catalytic poison could be submitted to a powerful process of reduction. Although capable of extraordinarily wide application, this process is nevertheless subject to certain limitations and disadvantages. Thus, only those substances which possess an appreciable vapour pressure at the necessary temperature of reaction, and give products of similar volatility, can be treated in this way. Occasionally, also, hydrogenation is incomplete, either on account of slowness of reaction or of insufficient concentration of Hydrogen at the ordinary pressure.

Sabatier supposed that his metal catalysts exerted their action by virtue of an unstable hydride, which alternately formed and passed on its Hydrogen to the substance undergoing reduction. In spite of this view, or possibly deterred by his observation that deposition of liquid on the catalyst impaired its activity, Sabatier did not extend his investigations to hydrogenation with Nickel, or other finely-divided metals, in liquid media. This advance was due to Ipatiev, who, generalising several isolated observations by Fokin, hydrogenated liquids and substances in solution by suspending a catalyst in the liquid and heating with Hydrogen at high pressure.

The sensitivity of metals to anticatalytic influences is also a great disadvantage in the Sabatier and Senderens method, which becomes much less serious, as Ipatiev has shown, when increased pressures of Hydrogen are employed. For example, Hydrogen at the ordinary pressure can only reduce the aromatic nucleus in contact with Nickel that has been scrupulously protected from poisons both in preparation and use. Nickel, can, however, be reduced from its oxide by unpurified Hydrogen, made from Zinc and Hydrochloric acid, and yet effect the hydrogenation of Benzene if a sufficient pressure of Hydrogen is applied (*J. Russ. Phys. Chem. Soc.*, 1914, 46, 302).

Fokin then showed that reduction of unsaturated substances could be effected in solution at much lower temperatures and pressures than those employed by Ipatiev, by using the catalysing metal in a colloidal or finely-divided, active form. Powerful effects were obtained with Nickel and Cobalt, but Platinum and Palladium-black, and colloidal solutions of these metals, were especially energetic, and often induced rapid hydrogenation at the ordinary temperature and pressure. Fokin's methods were generalised by Paal, and independently by Skita, using colloidal Platinum and Palladium, and by Willstätter, using Platinum and Palladium-black, and processes of hydrogenation were developed of almost universal application, and requiring only ordinary or slightly elevated temperatures and pressures of Hydrogen.

Ipatiev's Researches

In 1901, the Russian chemist Ipatiev commenced a long series of researches on catalysis, and recorded the results in the *Berichte*, and the *Journal of the Russian Physical and Chemical Society*, under the titles "Pyrogenic Actions of Organic Compounds" (1901 to 1903), and "Catalytic Reactions at High Temperatures and Pressures" (1904 to 1914). In the first papers, Ipatiev studied the various changes that alcohols and other simple substances undergo when heated with various contact agents, adding much to the detailed records of catalytic dehydration, dehydrogenation, and degradation, steadily accumulating as the result of the simultaneous activity of Sabatier, Knoevenagel, and others. A natural diversion from these simple experiments—the study of the different effects produced by application of high pressures—opened a completely new field.

Experiments on hydrogenation were carried out by heating a substance for several hours in a suitable vessel with Hydrogen at high pressure, up to 130 atmospheres, in contact with a catalytic agent. The apparatus was very simple, a strong tube of 250 to 275 c.c. capacity, fitted with a pressure gauge and stirring mechanism,

and constructed of steel, or, in cases where absence of Iron was necessary, of Phosphor-bronze. About 25 grams of the substance to be reduced were placed in the tube with 2-3 grams of catalyst and Hydrogen up to 100-130 atmospheres pressure, that is, about 1 gram-molecule. The temperature was then raised in some cases to 400° C., whereupon the pressure increased sometimes as much as $2\frac{1}{2}$ -3 times, that is, to 250-300 atmospheres, according to the temperature employed. The progress of hydrogenation was followed by observing the fall of pressure.

The material of the apparatus in some cases exerted a considerable influence in promoting, or altering, the reaction. For example, in the presence of Copper oxide and in an Iron tube, Trimethyl ethylene, $(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CH}_3$, was completely converted into iso-Pentane, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_3$, in 12 hours by Hydrogen at 200 atmospheres and 300° C., whereas when a Copper tube was used instead, the reaction was only one-third complete even after 28 hours. Likewise in a Phosphor-bronze apparatus, in presence of Copper, the reaction was incomplete unless Iron turnings were also added, when hydrogenation proceeded to completion. It must be noted that in an Iron tube, and in absence of Copper, no hydrogenation occurred under the same conditions (*Ber.*, 1910, 43, 3387; *J. Russ. Phys. Chem. Soc.*, 1910, 42, 1557). Similar results were obtained with certain hydroaromatic bodies.

The hydrogenating catalysts first used were finely-divided metals, especially Nickel, Iron, and Copper, and, in several cases, Palladium, Zinc, and Aluminium. The important observation was then made that oxides of Nickel were more powerfully active than finely-divided reduced Nickel itself, the most energetic being Nickelic oxide, then Nickel oxide, and lastly the free metal. It was also shown that the activity of Nickel in all its forms was greater when water, either free or combined, was present, and that the chemical activity of Nickel or Nickel oxide towards oxidation or reduction was modified similarly. Thus, reduction of the oxides of Nickel, as well as oxidation of the finely-divided free metal, occur at lower temperatures if water in some form is present. For example, Nickelic oxide is reduced by Hydrogen at atmospheric pressure at 190-200° C., while Nickelous oxide requires a temperature higher than 200° C., unless Hydrogen at high pressure is used, when reduction of Nickelous oxide commences at 172° C. If, however, all the water has been eliminated from these oxides by previous prolonged heating, then the temperatures at which reduction starts are much higher and the catalytic activities both of the oxides and the metal reduced therefrom are much less. On this evidence, supported also by later experiments, Ipatiev argued that the active catalytic agent in hydrogenation by his method, using a Nickel catalyst, was Nickel

oxide, promoted by the presence of water. Active finely-divided reduced Nickel always contained oxide and water, and in Ipatiev's view the action in hydrogenation consisted in the Hydrogen first reducing the oxide to metal and water, which in the nascent state interact with one another, reproducing oxide and nascent Hydrogen which rapidly hydrogenates any reducible substance present. Hence the function of a catalyst is to transform heat energy into chemical energy, thereby altering the limits of a reaction, and considerably exceeding the function assigned by Ostwald, Bredig, and others, that it merely increased the rate of reaction (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1; *J. pr. Chem.*, 1908, II, 77, 513). Sabatier contested this view, and explained the superior activity of the oxides by suggesting that the first effect of Hydrogen is to reduce them and that the "nascent" metal formed *in situ* possesses a maximum activity. Ipatiev showed, however, that even after prolonged use in hydrogenation, a Nickel catalyst still contained much Oxygen, presumably combined as oxide. Other investigators (*q.v.*) have postulated the existence of a suboxide, and ascribed to this the catalytic properties of Nickel.

Hydrogenation by Ipatiev's method generally yields the same products as are obtained by the method of Sabatier and Senderens, but on account of the longer period of contact with the catalytic agent at a high temperature bye-reactions frequently are more pronounced.

Ethylene, and Ethylenic Compounds

In the absence of contact agents, and at ordinary pressure, Ethylene is moderately stable at temperatures up to 600° C. Ipatiev was the first to show that at higher pressures Ethylene easily polymerises, forming gaseous and liquid products (*J. Russ. Phys. Chem. Soc.*, 1906, 38, 63; 1911, 43, 1420). At 70 atmospheres, this commences at 325° C., and is very fast at 380–400° C., the pressure diminishing at the rate of 5 atmospheres per minute. The liquid product formed contains paraffins (Pentane, Hexane, etc.), olefines (Amylene, Hexylene, etc.), Naphthenes, and oils boiling above 280° C., but no Benzene or derivatives. Alumina, Aluminium chloride, and Zinc chloride are catalysts for polymerisation of Ethylene (*Ber.*, 1913, 46, 1748). isoButylene under the same conditions also polymerises, giving corresponding products.

Unsaturated linkages between Carbon atoms are easily saturated by Ipatiev's method, using Nickel, Copper, or oxides of these metals, Platinum, Palladium, or Iron as catalysts.

Ethylene with excess of Hydrogen at 60 atmospheres and 180° C. is easily reduced by contact with Copper oxide to Ethane. Using Nickel oxide as catalyst, some Ethane is always broken down into Methane (*Ber.*, 1909, 42, 2089).

Trimethylethylene, $(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CH}_3$, at 300°C . in an Iron tube with Hydrogen at 100 atmospheres and in contact with Copper or Copper oxide, gives isoPentane, with a little tertiary Amyl alcohol. This reaction does not occur at the ordinary pressure, Copper usually not exerting any hydrogenating action by the Sabatier and Senderens method unless the ethylenic linkage is attached to at least one Methylene (CH_2) group. Copper fails to effect reduction of the partially hydrogenated aromatic nucleus (*e.g.*, Cyclohexene) even by the Ipatiev method.

As in the Sabatier and Senderens method, Copper catalysts possess certain advantages in that their action is milder, this enabling more easily-reducible groupings (*e.g.*, the Ethylenic linkage) to be reduced without attacking other groups in the same molecule. Thus, in the case of Sodium cinnamate, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COONa}$, at 300°C ., Nickel oxide gives β -Cyclohexyl sodium propionate, $\text{C}_6\text{H}_{11}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COONa}$, while Copper oxide gives quantitatively β -Phenyl sodium propionate, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COONa}$. Finely-divided reduced Copper is less active than Copper oxide, and does not, as a rule, completely reduce Sodium cinnamate (*Ber.*, 1909, 42, 2097).

Hydrogen at high pressure in contact with Nickel or Nickel oxide reduces ethylenic linkages in any compound. Cyclohexene easily passes quantitatively to Cyclohexane. Oleic acid at 100°C ., with Nickel or Cobalt powder, is not appreciably reduced under 26 atmospheres pressure, but at 60 atmospheres in 12 hours is completely reduced to Stearic acid. Liquid unsaturated oils likewise give solid fats (Fokin, *J. Russ. Phys. Chem. Soc.*, 1906, 38, 419, 855). Under the same conditions, Dimethyl allyl carbinol is reduced to Dimethyl propyl carbinol, and Mesityl oxide at 140 – 150°C . to Methyl isobutyl ketone, with a little of the corresponding alcohol.

The Ipatiev method, with modifications, has been used in hydrogenation of oils. With Nickel or Nickel oxide, and Hydrogen at sufficient pressure, all unsaturated linkages are completely reduced and the action of catalytic poisons can be largely countered by increased pressure.

Palladium reduced from its chlorides by action of a formate is an active catalyst at comparatively low temperatures. Methyl ethyl acrolein, $\text{C}_2\text{H}_5\cdot\text{CH}:\text{CH}\begin{smallmatrix} \text{CH}_3 \\ \text{CHO} \end{smallmatrix}$, at 110°C ., in 2 or 3 days gives Methyl pentanol. Mesityl oxide at 110°C . in 2 days gives Methyl isobutyl ketone, which can be further reduced by Nickel at 145°C . to isoButyl methyl carbinol.

Aldehydes and Ketones

In presence of Nickel or its oxides, Iron, Palladium, Copper oxide, and sometimes finely-divided metallic Copper or Zinc, the

carbonyl group of aldehydes and ketones is reduced, with formation of alcohols or (in the case of aromatic substances) of hydrocarbons.

The reduction of aliphatic aldehydes and ketones to primary or secondary alcohols, respectively, is reversible at temperatures where Nickel, Copper, or Iron exerts a rapid action. Thus, if Acetone is heated to 400–420° C. with Hydrogen at a pressure of 103 atmospheres, equilibrium is attained in about 20 hours in contact with Iron, and 25 per cent. of isoPropyl alcohol is formed, 50 per cent. of Acetone being recovered unchanged. A similar mixture is obtained by reacting upon isoPropyl alcohol under the same conditions (*Ber.*, 1907, 40, 1270). isoValeric aldehyde is similarly reduced till the reverse change produces a state of balance, but the alcohol formed is partially dehydrated to Amylene. isoButyl aldehyde similarly is reduced, giving at 350° C. 70 per cent. of the alcohol at the equilibrium point.

If Nickel is used instead of Iron, reduction commences at as low a temperature as 210–220° C., while the reverse is not appreciable below 220–230° C. The equilibrium would therefore appear to correspond very closely with complete reduction at temperatures below 220° C. in the cases of the simple aldehydes, but up to 250° C. good yields of the alcohol can be obtained from isoButyric or isoValeric aldehydes.

Aliphatic ketones give a similar state of balance. With Nickel or Nickel oxide at 200° C., they are changed almost completely into secondary alcohols. About 280° C., their transformation is limited by dehydrogenation, which more and more predominates as the temperature is raised. Thus, in 2 hours at 200° C., Acetone is almost completely reduced to isoPropyl alcohol, Methyl ethyl ketone to Methyl ethyl carbinol, and Methyl isobutyl ketone to Methyl isobutyl carbinol. At higher temperatures, a state of balance is produced, along with more or less decomposition. At 300° C. Acetone fails to give isoPropyl alcohol, because in contact with Nickel the latter is resolved into water and Propane, or lower saturated hydrocarbons.

Oxygen in a side-chain attached to an aromatic nucleus, whether in the form of an alcoholic hydroxy-group or an aldehydic or a ketonic carbonyl group, is completely reduced, as in the Sabatier and Senderens method. Benzaldehyde at 200° C., with Nickel or Nickel oxide, gives Toluene and Methyl cyclohexane, and at 280° C. in 12 hours, Toluene and Dibenzyl, with much resin. Using Iron at 280° C. and Hydrogen, as before, at 100 atmospheres, water, Toluene, Dibenzyl, and resin are formed. It is probable that in each case the alcohol is the first product of reduction, as in the case of aliphatic carbonyl compounds, and that this then breaks down into the hydrocarbon products. This view is confirmed by treating

Benzyl alcohol in the same way, when similar products are produced (*Ber.*, 1908, 41, 993).

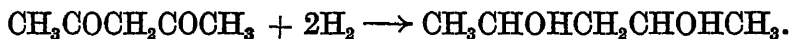
As in the Sabatier-Senderens method, aromatic ketones generally yield a saturated hydrocarbon containing the same number of carbon atoms. Thus, using a Nickel catalyst, Benzophenone gives Diphenyl methane, and Benzoin gives Dibenzyl.

Iron, as usual, is a less active catalyst than Nickel, but at 350–400° C. brings about the reduction of aliphatic aldehydes and ketones to alcohols. At such temperatures, equilibrium in the reaction is usually attained with much unreduced aldehyde or ketone still present, and decomposition is more considerable. Acetaldehyde is mainly resinified, and partly converted into Methane and Carbon monoxide.

Copper oxide is often applicable. For example, Acetone is not hydrogenated in an Iron tube at 280–300° C. under a high Hydrogen pressure: unless Copper, or Copper oxide (which becomes reduced to the metal during the process) is also present. A 65 per cent. yield of isoPropyl alcohol, is then obtained, further conversion being stopped by the reverse change (*Ber.*, 1911, 44, 3459).

Zinc dust also effects hydrogenation of Acetone at 100 atmospheres Hydrogen pressure, and produces a 50 per cent. conversion into isoPropyl alcohol. With a lower Hydrogen pressure (40 atmospheres) and a temperature of 300° C., the change is almost complete in the reverse direction.

Palladium is active at considerably lower temperatures. Acetyl acetone in 6 hours is reduced to the corresponding glycol,



If Nickel oxide is used, which requires a rather higher temperature, the product obtained is Methyl propyl ketone, probably formed by the glycol first passing to an internal anhydride, $\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_3$,



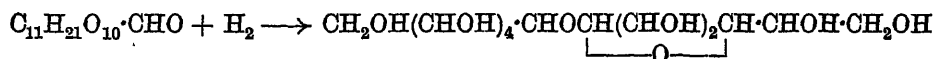
which isomerises to Methyl propyl ketone, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$. In other cases also, the activity of Palladium at a lower temperature is an

advantage. Thus, β -Methyl β -ethyl acraldehyde, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$, with a Nickel catalyst at 130° C. gives mainly a mixture of condensation products with only a little alcohol. Palladium at 110° C., on the other hand, with Hydrogen at 110 atmospheres, gives almost entirely γ -Methyl *n*-amyl alcohol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$.

Citral, shaken under Hydrogen pressure with Palladium at 110° C., or active reduced Nickel containing Nickel oxide at 140° C., is reduced to a mixture of Dimethyl octanol and Dimethyl octane—

by reduction of the aldehyde and partial elimination of the resulting hydroxyl group. With continuous stirring, however, the reaction proceeds smoothly to completion, and only the Decanol is obtained. Geraniol in the same way gives Decanol, with a little Decane (*Ber.*, 1912, 45, 3218).

Sugars are similarly reduced. With Palladium at 110° C., or Nickel or Nickel oxide at 130–135° C., a 20–30 per cent. aqueous-alcoholic solution of Lævulose is partially reduced to *d*-Mannitol, Dextrose to *d*-Sorbitol, and Lactose to Dulcitol (*J. Russ. Phys. Chem. Soc.*, 1913, 44, 1002). By using a weakly active Nickel-Nickel oxide catalyst (prepared at 500° C.), and carrying out the reduction at 120° C. in aqueous-alcoholic solution, Senderens has isolated as an intermediate reduction product the alcohol "Lactositol," corresponding to the aldehyde Lactose,



Lactositol is hydrolysed by dilute acids to a mixture of Sorbitol and Galactose. If a more active catalyst is used in the hydrogenation, hydrolysis and complete reduction occur simultaneously, and the only products are Dulcitol and Sorbitol, without any intermediate (*C.R.*, 1920, 170, 47).

The Aromatic Nucleus

In the presence of Nickel or oxides of Nickel, the aromatic nucleus can be completely hydrogenated in all cases by Hydrogen under pressure, while Copper, Aluminium, or Iron, even at very high pressures, are quite inert. Nickelic oxide is more active than Nickelous oxide, and many times more active than the finely-divided reduced metal.

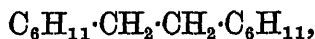
Benzene at 250° C. in 1½ hours gives Cyclohexane quantitatively, no unreduced Benzene remaining. This is therefore the best method of preparing pure Cyclohexane. At 300° C., Cyclohexane dissociates into Benzene and Hydrogen, simultaneously decomposing into paraffins, olefines, and carbon.

Diphenyl, $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5$, and Dibenzyl, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$, at 250° C. give, respectively, Dicyclohexyl, $\text{C}_6\text{H}_{11}\cdot\text{C}_6\text{H}_{11}$, and Dicyclohexyl ethane, $\text{C}_6\text{H}_{11}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_{11}$. Phenol at 245° C. in 4 hours is reduced to Cyclohexanol, with more or less Cyclohexanone; Hydroquinone at 200° C. to para-Dihydroxycyclohexane; and Diphenyl ether at 230° C. in 12 hours to a mixture of Dicyclohexyl ether, $(\text{C}_6\text{H}_{11})_2\text{O}$, Cyclohexanol, and Cyclohexane (*Ber.*, 1908, 41, 1001). Phenol also gives a certain amount of these last-named products by hydrogenation and dehydration.

Aniline in 50 hours at 220–230° C. is converted into a mixture of

40–50 per cent. of Cyclohexylamine, and 10 per cent. each of Dicyclohexylamine and Cyclohexylaniline. Diphenylamine under the same conditions gives mainly Dicyclohexylamine (*Ber.*, 1908, 41, 991).

Side-chains, containing Oxygen, attached to an aromatic nucleus, are in all cases completely reduced in contact with Nickel and Hydrogen at high pressure, $\cdot\text{H}$ taking the place of the $\cdot\text{OH}$ group, and :CO being replaced by :CH_2 , while the nucleus itself is slowly hydrogenated. Thus, Benzoin, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CHOH}\cdot\text{C}_6\text{H}_5$, is reduced to Dibenzyl, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$, and Dicyclohexyl ethane,



and para-Xylyl alcohol, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CH}_3 \\ < \\ \text{CH}_2\text{OH} \end{smallmatrix}$ to para-Hexahydroxylene.

Phenols with unsaturated side-chains can be reduced in the side-chain without attacking the ring by means of Copper oxide at 270–300° C., or by Nickel at 95° C. The ring is not attacked under any conditions in presence of Copper, and with Nickel requires a temperature of at least 190° C. Polyphenols, which can only be reduced slowly on account of the necessity of a low temperature, cannot be more easily dealt with in the form of their ethers, since methoxy-groups tend to be eliminated (*Ber.*, 1913, 46, 3589; *J. Russ. Phys. Chem. Soc.*, 1913, 45, 1829; 1914, 46, 470). Thus, Anethole, $\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$, with Nickel at 95° C., and Hydrogen at 50 atmospheres is reduced in 4 hours to Dihydroanethole (para-Anisyl propane, $\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{C}_3\text{H}_7$), and this, on further treatment at 200° C. for 20 hours, is hydrogenated, with loss of the methoxy-group to Cyclohexyl propane.

Guaiacol, with Nickel oxide at 220–240° C. and Hydrogen at 100 atmospheres, yields a mixture of Hexahydroguaiacol (2-Methoxycyclohexanol), Cyclohexane, and Cyclohexanol. Anisole under the same conditions gives Cyclohexene, Cyclohexanol, and Hexahydroanisole. The diethyl ether of Catechol similarly gives 50 per cent. of the hexahydro-body, $\text{C}_6\text{H}_{10}(\text{OC}_2\text{H}_5)_2$, apparently in both cis- and trans-modifications, and Cyclohexane, while the dimethyl ethers of Resorcinol and Hydroquinone give, in addition to the hexahydroethers, some Cyclohexane and Methoxy-cyclohexane, respectively. The behaviour of the terpene derivatives which contain unsaturated linkages and methoxy-groups is similar, as, for example, Eugenol and isoEugenol, which at 92° C. in 2–3 hours give Dihydroeugenol, and at 195° C., for a further 7 hours, a mixture of 3-Methoxy-4-hydroxycyclohexyl propane and 3-Methoxy-cyclohexyl propane. Eugenol methyl ether (3 : 4-Dimethoxy-1-allyl benzene) in the same way gives first the corresponding Dimethoxy phenyl propane, and finally Dimethoxy-cyclohexyl propane. Safrole and isoSafrole under similar conditions give first Dihydrosafrole (3 : 4-Methylene dioxy-

phenyl propane), and on further reduction, 3(or 4)-Methoxy-cyclohexyl propane.

Aromatic acids, which cannot in general be reduced by the method of Sabatier and Senderens, may be hydrogenated by Hydrogen under pressure to the corresponding cyclohexyl carboxylic acid (*Ber.*, 1908, 41, 1001). The free acid, however, may not be used, since it attacks the catalyst, and esters in many cases give unsatisfactory results, as, for example, Ethyl phthalate, which in contact with Nickel oxide and Hydrogen at high pressure gives a mixture of ortho-Toluic, Phthalic, and Benzoic acids and Carbon dioxide. The alkali salts, on the other hand, react fairly smoothly. Thus, Potassium phthalate, $C_6H_4(COOK)_2$, when heated with Nickel oxide in Hydrogen at 100 atmospheres pressure, gives a good yield of trans-1:2-Cyclohexane potassium dicarboxylate, $C_6H_{10}(COOK)_2$, the most convenient method of preparing this substance. When Potassium phthalate is subjected to similar treatment in a current of Hydrogen at the ordinary pressure, or when high-pressure Hydrogen is employed but no catalyst, no action occurs.

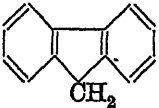
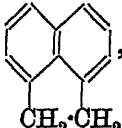
Sodium cinnamate under the same conditions gives Cyclohexyl sodium propionate, $C_6H_{11} \cdot CH_2 \cdot CH_2 \cdot COONa$, Potassium benzoate at $280^\circ C.$ gives a 40 per cent. yield of the hexahydro-benzoate, but in this case the Sodium salt is reduced more easily and at $300^\circ C.$ yields 50 per cent. Above $320^\circ C.$, large quantities of Methane are formed. The two Naphthoic acids behave differently when hydrogenated at 100 atmospheres in contact with Nickel oxide at $360^\circ C.$ Using the Sodium salts, the α -acid gives Tetrahydronaphthalene, while the β -acid gives Tetrahydro- β -naphthoic acid, and then, on repeating the action, a mixture of Decahydronaphthalene and Decahydro- β -naphthoic acid (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 1414; *Ber.*, 1909, 42, 2097).

Polynuclear Hydrocarbons

All polynuclear hydrocarbons can be completely hydrogenated by Ipatiev's method, using Nickel or Nickel oxides, even when by the method of Sabatier and Senderens they are only partially reduced. Decomposition, however, is often more marked. Generally several stages of reduction can be isolated thus: Naphthalene with Nickel at $250^\circ C.$ and Hydrogen at 120 atmospheres is reduced in two stages, giving first the tetrahydride, and finally the decahydride. α - and β -Naphthols, however, give the α - and β -decahydro-derivatives. Quinoline similarly is reduced in two stages, first to the tetrahydride, then to the decahydride (*Ber.*, 1908, 41, 991).

Anthracene and Phenanthrene are reduced in three stages. The former, at 260 – $270^\circ C.$ and Hydrogen at 120–130 atmospheres during 10–16 hours, is reduced first to the tetrahydride, next to the

decahydride, and finally to the perhydride. Some destruction, however, takes place. For reduction of Phenanthrene a much higher temperature, 400°C ., is necessary, but even so, little or no destruction occurs, and good yields result. In the first stage, a mixture of Dihydro- and Tetrahydro-phenanthrenes is formed, the second stage is the Octahydride, and the final the Perhydride (Ipatiev, Jakovlev, and Rakitin, *Ber.*, 1908, 41, 996).

Fluorene, , and Acenaphthene, , are reduced in

two stages, at 285°C . and 120 atmospheres of Hydrogen, the former to (1) Decahydrofluorene and (2) Perhydrofluorene, $\text{C}_{13}\text{H}_{22}$, and the latter to (1) Tetrahydro-acenaphthene and (2) Decahydro-acenaphthene.

Retene (1-Methyl-4-isopropyl phenanthrene) in the same way gives (1) Decahydro-retene and (2) Perhydro-retene, $\text{C}_{18}\text{H}_{32}$ (*Ber.*, 1909, 42, 2092).

Indene, in contact with Nickel oxide at $250\text{--}260^{\circ}\text{C}$. and Hydrogen at 110 atmospheres, gives at once Octahydrindene (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 994; cf. Padoa and Fabris using the Sabatier and Senderens method).

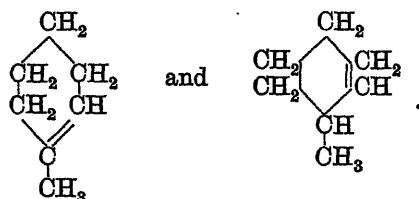
Terpenes and Related Substances

The reactions already described are applicable directly to the Terpenes. In those containing both a double linkage and a carbonyl group, using a Nickel oxide catalyst, the former is saturated at a temperature of $220\text{--}240^{\circ}\text{C}$., irrespective of whether it occurs in a partially reduced ring or in a side-chain. The carbonyl group requires a higher temperature for reduction, about $260\text{--}280^{\circ}\text{C}$., preferably nearer the lower limit, especially in the Menthhol series, in order that decomposition may be minimised. Thus, Carvone at $220\text{--}240^{\circ}\text{C}$. gives Carvomenthane, and at 280°C . Carvomenthol. Pulegone at the lower temperature gives Menthone, and at the higher Menthane (*Ber.*, 1911, 44, 3461).

Camphor is reduced to Borneol at $320\text{--}350^{\circ}\text{C}$. in contact with Nickel oxide, and Hydrogen at high pressure. Limonene at $300\text{--}320^{\circ}\text{C}$. gives a dihydride, with decomposition to Methane. Pinene at 265°C . gives the dihydride, and at 300°C . Menthane.

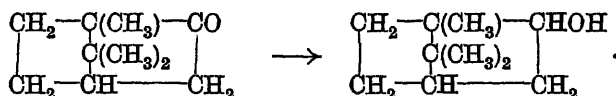
Such changes can also be accomplished in most cases by other catalysts. Thus, in contact with Copper, Pinene is reduced to the dihydride, and Camphene to a mixture of isomeric dihydrides, one a solid, the other a liquid. Citral and Geraniol, heated with Palladium and Hydrogen under high pressure, give Decanol.

Experiments with hydroaromatic substances and terpenes showed that the effect of two different types of catalysts acting together (a dehydrating and a hydrogenating) is very much greater than when either acts separately (*Ber.*, 1912, 45, 3205; *J. Russ. Phys. Chem. Soc.*, 1912, 44, 1675). Thus, Hexahydro ortho-cresol, $\text{CH}_3 \cdot \text{C}_6\text{H}_{10} \cdot \text{OH}$, in presence of Alumina at 350°C . and Hydrogen under pressure, gives a mixture of two isomeric Methyl cyclohexenes:—



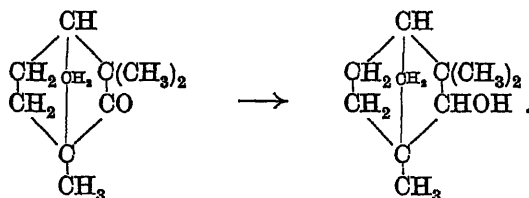
In the presence of Copper oxide and Alumina together, however, the reaction takes place at 240°C . with 20 atmospheres Hydrogen pressure and gives almost exclusively the former product, $\Delta^{1:2}$ -Methyl cyclohexene.

Camphor, in presence of Nickel oxide and Hydrogen at high pressure, requires a temperature above 300°C . to effect reduction to Borneol:—



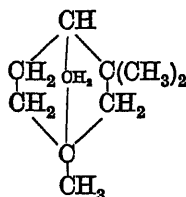
Borneol is stable in contact with Alumina until a temperature of $350\text{--}360^\circ \text{C}$. is reached. Even at this point reaction is slow, and does not proceed beyond the formation of Camphenes by dehydration. If, however, both catalysts are used together, then Camphor at $212\text{--}220^\circ \text{C}$., with Hydrogen at 110 atmospheres, is reduced directly—and presumably *via* these intermediate steps—to isoCamphene.

Fenchone, in contact with Nickel oxide at 240°C . and Hydrogen at 110 atmospheres, is reduced in 20 hours to Fenchol:—



Dehydration of Fenchol with Alumina as catalyst is very difficult, and gives only small yields of Fenchene at $210\text{--}255^\circ \text{C}$. If, however, a mixed catalyst of Alumina and Nickel oxide be used at 215°C . and 110 atmospheres of Hydrogen, these reactions occur simul-

taneously, and Fenchone is directly and nearly completely reduced in 12–14 hours to Fenchane.



Camphene, in presence of Nickel oxide at 240° C. and Hydrogen at high pressure, gives a solid isoCamphane. Attempts to prepare Camphene by dehydration of Borneol with Alumina at 350–360° C. gave very little of a liquid Camphene, with much oxidation, the reaction being slow. When, however, Borneol was treated at 215–220° C. under 110 atmospheres of Hydrogen in presence of the mixed catalysts, isoCamphane was at once obtained. isoBorneol under the same conditions also gave isoCamphane, even though when heated with Alumina alone at 350–360° C. isoBorneol gives mainly a condensation product and only small quantities of a solid Camphene.

The reduction of cyclic ketones to saturated hydrocarbons is also easier in contact with the mixed hydrogenating and dehydrating catalysts, and takes place at a lower temperature than either of the individual reactions by which, it may be presumed, the final result is attained. Thus, at 200° C., in presence of Nickel oxide and Alumina, Carvomenthone is easily reduced by Hydrogen at high pressure to Menthane.

When Copper oxide instead of Nickel oxide is mixed with Alumina, terpene alcohols yield unsaturated hydrocarbons, since in presence of Copper dehydration with Alumina takes place at a much lower temperature—220° C. instead of 360° C.—which is below the point at which hydrogenation of the double linkage is brought about by Copper. Hence whereas Nickel oxide and Alumina give the saturated hydrocarbon, Copper oxide and Alumina yield the unsaturated, thus: Borneol at 200–220° C. and Hydrogen pressure at 50 atmospheres in presence of Copper oxide and Alumina gives a mixture of solid and liquid Camphenes; isoBorneol under the same conditions gives only solid Camphene; while Nickel oxide effects the further reduction of either of these products to isoCamphane.

Colloidal Metals as Catalysts

When a reaction is induced by contact with a catalytic surface, its rate is dependent upon the area of surface exposed. For “contact” or heterogeneous reactions, therefore, the finer the state of division of the catalyst the faster will be the action produced by a

certain definite quantity. The limit of subdivision is obtained by solution, when, as cryoscopic determinations show, a body is generally resolved into individual molecules and the solution is regarded as homogeneous. The characteristic surface actions of bodies are not, however, manifested by particles of molecular dimensions, and any catalytic action that then occurs depends upon other properties of the catalyst. The extreme limit of subdivision consistent with surface action is obtained when a body is dispersed in colloidal solution, and in this state bodies frequently exhibit their most intense catalytic action.

Various methods are available for preparation of colloidal metal or metallic hydroxide solutions. The most convenient and most generally applicable consists in decomposing a dilute aqueous solution of a metallic salt by addition of a reducing agent, or base, under such conditions that the free metal or hydroxide liberated is so finely divided that it remains in colloidal suspension. This method has been exhaustively investigated by Gutbier, and simultaneously by Paal, who added solutions of the following reducing agents: Sulphur dioxide, Hypophosphorous acid, Formaldehyde, Phenyl hydrazine, Sodium amalgam, but especially Hydrazine hydrate or Hydroxylamine to dilute solutions of metallic salts, and obtained hydrosols of Gold, Silver, Copper, Bismuth, Lead, Mercury, and the Platinum metals and from Selenious and Telluric acids, colloidal solutions of Selenium and Tellurium (Gutbier, *Z. anorg. Chem.*, 1902, 31, 448; 32, 51, 91, 106, 347; Gutbier and Resenscheck, *Z. anorg. Chem.*, 1904, 39, 112; 40, 264; Gutbier and Hofmeier, *J. pr. Chem.*, 1905, ii, 71, 358; *Z. anorg. Chem.*, 1904, 42, 117; 1905, 44, 225; Paal, *Ber.*, 1902, 35, 2224, 2236).

Colloidal solutions so made were not, however, very stable, and tended to flocculate or deposit the colloid in a coarser, precipitated, form. Dissolved impurities much influenced the stability of colloidal solutions, especially dissolved electrolytes (acids, salts, etc.), which very greatly increased the tendency to flocculate, and easily soluble stable colloids (gum arabic, proteid substances, starch), which greatly reduced this tendency. This property of "protective colloids" to increase the stability of metal and hydroxide hydrosols was widely used by Paal, Skita, and other investigators, who employed such solutions for catalytic purposes.

Gutbier treated very dilute solutions of Platinic, Palladious, Iridium, or Auric chlorides with slight excess of Hydrazine hydrate in presence of gum arabic. The resulting solutions were filtered and dialysed, and when all electrolytes had diffused away, concentrated by gentle heat *in vacuo*. These sols were stable in light but precipitated the metal with Barium sulphate or animal charcoal. They could be evaporated to dryness at a low temperature over

strong Sulphuric acid, and the solid remaining was easily soluble in warm water. Gutbier later developed the use of starch as a protective colloid (*Koll. Chem.*, 1913, 5, 211, 244).

The application of colloidal hydrogenating catalysts and the use of protective colloids to stabilise them was developed by Paal. In an investigation dealing with "The Action of Alkaline Hydroxides on Egg-albumin" (*Ber.*, 1902, 35, 2195) Paal isolated the two compounds designated "Protalbic" and "Lysalbic" acids. Kalle and Co. afterwards patented the large-scale preparation of these protective colloids (D.R.-PP. 170433, 170434).

When albumen is heated at 100° C. for 1 hour with 3 per cent. caustic Soda solution, Ammonia is evolved and the solid coagulum which first forms nearly redissolves. On acidifying the solution with Acetic acid, Protalbic acid is precipitated. This is filtered, freed from salts by dialysis and from water by washing with alcohol, and dried by gentle heat *in vacuo*. Protalbic acid is a white powder easily soluble in aqueous Acetone or Acetic acid and in acids and alkalis. Its composition varies between the following limits: Carbon 53.5–54.0 per cent.; Hydrogen 7.3–7.5 per cent.; Nitrogen 14.3–14.6 per cent.; while small quantities of Sulphur are present. The Sodium, Potassium, Calcium, and Barium salts, made by dissolving the acid in slight excess of the hydroxides, removing the excess by dialysis, and evaporating, are white powders.

Lysalbic acid remains in the mother-liquor after precipitating the Protalbic acid, and is isolated by evaporating to small bulk on a water-bath, acidifying with Sulphuric acid, and pouring the concentrated solution into Alcohol. It is a white powder of composition: Carbon 50.5–51.2 per cent.; Hydrogen 6.6–6.9 per cent.; Nitrogen 15.1–15.7 per cent.; with a little Sulphur, easily soluble in water to an acid solution which gives the biuret protein reaction. After purifying by reprecipitation from Alcohol and drying over Sulphuric acid, cryoscopic measurements indicate a molecular weight of 818–838; and after drying at 100° C., 1171–1187.

Paal prepared liquid hydrosols of Silver, Gold, Copper, Osmium, Iridium, Platinum, and Palladium by adding Protalbic or Lysalbic acid, or a soluble salt of one of these stabilisers, to a dilute solution of a salt of one of the metals, followed by a suitable reducing agent. For Gold chloride, Formaldehyde was used; for Silver, Platinum, and Palladium, Hydrazine hydrate; and for Iridium, Sodium amalgam or Formaldehyde. The colloidal solution so formed was freed from "crystalloids" by dialysis, and concentrated.

The product from the chlorides of Platinum or Palladium or Chloroplatinic acid, when concentrated on a water-bath and dried at 100° C., finally *in vacuo*, formed glistening scales which easily redissolved in water to a dark brown, opalescent solution of remark-

able stability (Paal and Amberger, *Ber.*, 1904, 37, 124). More recently, Paal and Amberger have used gaseous Hydrogen to reduce the chlorides of Platinum, Palladium, and Iridium, and Osmic acid. A swift current of Hydrogen was passed through a solution of Palladious chloride in water at 60° C. to which Sodium protalbate or lysalbate had been added. After dialysing the product until free from salts, it was evaporated and dried *in vacuo*. The black, glistening scales of the solid Palladium hydrosol readily gave a colloidal hydride of Palladium by warming to 60–110° C. in a current of Hydrogen. The hydride surrendered its Hydrogen in a current of Carbon dioxide at 130–140° C., but, Sodium protalbate retaining its protective properties at this temperature, the residue was still soluble in water to a colloidal solution of Palladium (*Ber.*, 1905, 38, 1398).

Reduction with Hydrogen is especially convenient when the colloidal solution is required for hydrogenation, since the reduction can be carried out concurrently with the subsequent reaction.

Colloidal Iridium and Osmium were also made. The best method of preparation of colloidal Iridium was described in *Ber.*, 1917, 50, 722. The solid hydrosol of Osmium, unlike those of Platinum, Palladium, and Iridium, slowly oxidised in air, giving the characteristic smell of the tetroxide. It was made by reducing an alkali osmate, in presence of Sodium lysalbate or protalbate, with Hydrazine hydrate or fine Aluminium. The colloidal Osmium oxide obtained by this treatment was purified from salts by dialysis, evaporated, dried *in vacuo* and the solid hydrosol completely reduced by warming in Hydrogen (*Ber.*, 1907, 40, 1392).

Colloidal oxides of Silver and Mercury were made by Paal by precipitating the protalbates or lysalbates of these metals and adding caustic Soda (*Ber.*, 1902, 35, 2206, 2219). The preparation of colloidal Copper and Cupric oxide was described by Paal and Leuze (*Ber.*, 1906, 39, 1545, 1550) and colloidal Selenium and Tellurium by Paal and Koch (*Ber.*, 1905, 38, 526, 534), while the colloidal Cupric oxide as made by Paal and Leuze was reduced to colloidal Cuprous oxide by Paal and Descheimer (*Ber.*, 1914, 47, 2195).

Kelber and Schwarz in their investigations on the regulated reduction of acetylenic derivatives used a catalyst which was prepared as follows: Palladium chloride was added to a protective solution made by heating Gluten with Acetic acid. The clear, dark brown solution so obtained was faintly basified with Ammonia, and Hydrazine hydrate slowly added in excess. When reduction was complete, the deep brownish-black solution was dialysed until free from chloride and evaporated to dryness *in vacuo*. Black, glistening lamellæ, containing about 17.2 per cent. of Palladium, were obtained,

easily soluble in water or glacial Acetic acid, forming a solution which was not flocculated by dilute mineral acids. Platinosols were made in the same way (*Ber.*, 1912, 45, 1946).

By using gum arabic as protective colloid, Skita obtained acid-stable hydrosols, and in his investigations on the hydrogenation of unsaturated aldehydes and ketones prepared the catalyst as follows: Palladious chloride and gum arabic were added to an aqueous-alcoholic solution of the aldehyde or ketone, and a current of pure Hydrogen was then passed (D.R.-P. 230724). The Palladious chloride was first reduced, forming colloidal Palladium, which then catalytically induced the hydrogenation first of the unsaturated linkage, and then in certain cases of the carbonyl group. On the other hand, when Palladious chloride and gum arabic were added to an unsaturated compound not containing a carbonyl group, and Hydrogen was passed, the metal separated as a precipitate and not in the colloidal form. In this condition, however, the metal possessed considerable activity and effected certain hydrogenations, as, for example, Camphene to Dihydro camphene, and β -Phenyl vinyl acetate, $C_6H_5 \cdot CH:CH \cdot O \cdot CO \cdot CH_3$ to β -Phenyl ethyl acetate,



but failed with more difficult hydrogenations such as that of a partially-reduced aromatic nucleus. The influence of the carbonyl group in causing the reduced Palladium to assume the colloidal form was attributed to formation of a double compound of the ketone or aldehyde with some of the Palladium chloride (see Zeisse, *Ann.*, 1840, 33, 29). From such a compound colloidal particles were supposed to be produced which influenced the separation of the rest in a similar form. This view was confirmed by dissolving Palladious chloride in a solution of gum arabic and reducing in Hydrogen at the ordinary temperature, when, if no colloidal Palladium was already present, the metal slowly precipitated, whereas if a small quantity of a Palladium hydrosol had been previously added the Palladious chloride rapidly reduced, and the metal remained in colloidal solution.

A colloidal solution of Palladium can, however, be made by reducing with Hydrogen a hot solution of Palladious chloride containing gum arabic.

Solutions of Palladious chloride or Potassium platinochloride, when mixed with gum arabic and treated with Sodium carbonate solution, give colloidal solutions of Palladious or Platinous hydroxide. By dialysing these solutions, and evaporating *in vacuo*, scaly residues of brown Palladious hydroxide or black Platinous hydroxide are obtained, which readily redissolve to colloidal solutions in water and are admirably adapted for catalytic purposes. These colloidal

hydroxide solutions when shaken with Hydrogen are easily reduced to colloidal metal, and evaporation *in vacuo* then gives black scales of the easily-soluble solid hydrosols of Palladium or Platinum. Colloidal solutions of Palladium or Platinum made either by direct reduction of the chlorides, or *via* the colloidal hydroxides, are stable even in boiling Acetic acid, and possess a high degree of catalytic activity, enabling (when sufficient is used) even the aromatic nucleus to be hydrogenated (Skita and Meyer, *Ber.*, 1912, 45, 3597, 3589).

The simplest procedure in hydrogenating an unsaturated compound is to add to a solution of Palladium or Platinum chloride containing gum arabic a few drops of colloidal Palladium or Platinum solution and then pass Hydrogen. The unsaturated substance, which may be already present or now introduced, is then easily reduced.

Kalle and Co. have a process for the preparation of colloidal Osmium and Ruthenium, and the hydroxides of these metals, as follows (D.R.-P. 280365 of 1913). The tetroxides OsO_4 and RuO_4 are mixed with a protective colloid, such as Sodium lysalbate or protalbate, and with Alcohol, and evaporated to dryness *in vacuo*. The Alcohol reduces the tetroxides to the tetrahydroxides, which are non-volatile, but which must be protected from reoxidation to the volatile tetroxides during the evaporation. The solid colloidal hydroxides obtained can then be reduced to the colloidal metals with Hydrogen at a low temperature.

The simplest method of preparing a colloidal solution of Platinum was described by Bredig, and consists in forming an electric arc between Platinum poles under the surface of pure ("conductivity") water, whereby the molecules of the Platinum are torn apart, or perhaps vaporised by the arc and suddenly chilled by the water, yielding particles of sufficient fineness to dissolve to a colloidal solution (*Z. Phys. Chem.*, 1900, 31, 271). Two short Platinum wires, 1 millimetre thick, are bound to the ends of two pieces of stout Copper wire covered with insulating material. Small glass tubes are slipped over both pieces of Platinum wire to cover them to within about 1 centimetre of the free ends. The Copper wires are then connected to the terminals of a 110-volt direct current circuit with a lamp in series to serve as a resistance. Pure water, distilled from alkaline permanganate in a silver retort, is placed in a dish and cooled externally with ice, while the Platinum points are first brought together beneath the surface and immediately drawn apart to form an arc. This is maintained for about 10 minutes, pulling the wires apart when they fuse together, or touching them momentarily when the arc breaks. The black solution of colloidal Platinum is then filtered, and a stabiliser added if it is desired to preserve it.

Colloidal Palladium is made similarly (Bredig and Fortner, *Ber.*, 1904, 37, 798).

The rates at which colloidal solutions of the Platinum metals induce the decomposition of Hydrogen peroxide were compared by Paal and Amberger (*Ber.*, 1907, 40, 2201). When the solutions were made by Paal's method, the order of activity was Osmium, Palladium, Platinum, Iridium, and entirely different from the order of activity of these colloids when prepared by Bredig's method.

Colloidal Nickelous oxide was prepared by Paal and Brünjes from Nickel sulphate solution in presence of sodium lysalbate or protalbate. After purification by dialysis, the solution was fairly stable, with a greenish-yellow colour, clear in transmitted light, and opalescent in reflected light. Evaporation *in vacuo* left brownish-yellow, brittle, transparent lamellæ, which redissolved in water (*Ber.*, 1914, 47, 2200).

Catalysts in colloidal form are very susceptible to anti-catalytic influences, and it may be partly on this account that many investigators have found their hydrogenating power capricious. Wallach observed that unsaturated compounds of the terpene class were easily hydrogenated in presence of colloidal Palladium, but that, unless pure, they soon rendered the catalyst inert (*Ann.*, 1911, 381, 51). Solvents show marked differences, Benzene being distinctly anticatalytic, Alcohol and Ether apparently normal, while Acetic acid in many reactions is a strong promoter.

Paal and Karl examined the influence that presence of other metallic compounds exerted towards the hydrogenating action of Platinum and Palladium. Whether present as the free metal, oxide, hydroxide, or carbonate, Aluminium, Iron, Copper, Zinc, Cadmium, Mercury, Tin, Silver, and Lead were anti-catalytic, and of the metals tested only Magnesium, Nickel, and Cobalt were without deleterious action (*Ber.*, 1911, 44, 1013; 1913, 46, 3069, 4010).

When mixtures of Hydrogen and Oxygen are shaken with colloidal solutions of Platinum or Palladium, active combination of the gases is induced. If, however, the reaction is carried out in a gas burette over Mercury, the action, brisk at first, gradually ceases owing to the poisonous action of the Mercury (Paal and Schwarz, *J. pr. Chem.*, 1916, ii, 93, 106). This is in accord with the observation that Mercury is able to displace adsorbed Hydrogen from finely-divided or colloidal Platinum (Paal and Steger, *Ber.*, 1918, 51, 1743).

The strong promoting influence of traces of Oxygen on the hydrogenating activity of the Platinum metals, which was exhaustively studied by Willstätter and Jaquet in connection with their researches using Platinum-black, was first observed by Böseken

and Hofstede (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, 20, 424). These investigators, using colloidal Palladium prepared by Skita and Meyer's method, noticed considerable irregularities in the rate of reduction of Cinnamic acid and its esters under apparently comparable conditions, which were traced to the presence of Oxygen, which was shown, even in small amounts, to exert a marked activation of the catalyst.

Reduction of Nitrogen Compounds

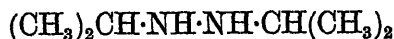
Nitrobenzene in an aqueous-alcoholic solution containing colloidal Palladium or Platinum is easily reduced at the ordinary temperature to Aniline on agitating in a current of Hydrogen (Paal and Amberger, *Ber.*, 1905, 38, 1406). This was confirmed by Paal and Gerum (*Ber.*, 1907, 40, 2209), who reduced Nitrobenzene both at the ordinary temperature and at 65–80° C., and showed that of the three actively catalytic metals Palladium was the most energetic, then Platinum, and thirdly Iridium. Silver and Osmium possessed a slight action, while Copper and Gold were inert. One preparation of colloidal Palladium, 3 years old, which had undergone some oxidation, was found to possess an exceptionally powerful catalytic action.

ortho-Nitro acetophenone, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_3$, and Nitrobenzene were reduced to their respective amido-compounds by Skita and Meyer (*Ber.*, 1912, 45, 3579), who also reduced Azobenzene, $\text{C}_6\text{H}_5\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_5$, first to Hydrazobenzene, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, and then to Aniline. In alcoholic solution, in presence of colloidal Palladium, and Hydrogen at 2 atmospheres, the first stage of this reduction is fast, while the second stage, that of Hydrazobenzene to Aniline, is comparatively slow (*Ber.*, 1912, 45, 3312).

Paal and Hartmann showed that a stabilised colloidal Palladium solution in presence of an easily reducible substance, such as Sodium picrate (which is reduced to 2 : 4 : 6-Triaminophenol), could be used as an absorbent for Hydrogen in gas analysis (*Ber.*, 1910, 43, 243). After eliminating all the other easily-absorbable gases, the mixture is shaken with Sodium picrate and Palladium hydrosol in an ordinary Hempel apparatus, when in a period varying from 10 to 120 minutes all the Hydrogen is combined. Satisfactory analyses of a number of mixtures containing all the common gases were carried out in this way.

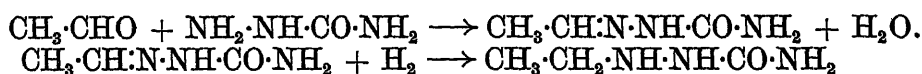
Mailhe, employing the Sabatier and Senderens method, attempted unsuccessfully to obtain substituted hydrazines by the graduated hydrogenation of ketazines (see page 215). With the much more sensitive control rendered possible by the use of colloidal catalysts in liquid media, this reduction can be effected. Using colloidal Platinum according to Skita's method, in aqueous solution containing enough Hydrochloric acid to neutralise the base formed, Lochte, Bailey

and Noyes obtained from Dimethyl ketazine, $(\text{CH}_3)_2\text{C}:\text{N}:\text{N}:\text{C}(\text{CH}_3)_2$, a 90 per cent. yield of sym. Di-isopropyl hydrazine,



(*J. Am. C.S.*, 1921, 43, 2597). isoButyraldehyde azine, and Dimethyl ketazine were also hydrogenated by Taipale (*Ber.*, 1923, 56 B, 954), and the results indicated that, using Platinum-black, the method could probably be applied generally, constituting therefore the best method of obtaining the difficultly accessible aliphatic hydrazines. Reduction was usually slow, and the yield in most cases did not exceed 60 per cent.: except in Acetic acid solution, when reduction was fast, and Dimethyl ketazine gave the hydrazine almost quantitatively. Primary and secondary amines, and Ammonia, were the usual bye-products, formed by reduction proceeding beyond the hydrazo-stage.

Semicarbazones of aliphatic aldehydes are also hydrogenated in Alcohol, or preferably glacial Acetic acid solution, in presence of Platinum-black. Semicarbazides are formed almost quantitatively, thus:—



(Taipale and Smirnoff, *Ber.*, 1923, 56 B, 1794).

Reduction of Ethylenic and Acetylenic Compounds

Hydrogenation at comparatively low temperatures and pressures in presence of colloidal metal catalysts was first demonstrated by Fokin (*J. Russ. Phys. Chem. Soc.*, 1907, 40, 276). Using the following catalysts: colloidal Platinum and Palladium, Platinum and Palladium-black, active finely-divided Nickel and Cobalt, Fokin reduced the following unsaturated to the corresponding saturated compounds by dissolving them in water or Alcohol, and submitting to the action of Hydrogen at varying temperatures and pressures: Oleic acid, the fatty acids from linseed oil, Allyl alcohol, Maleic acid. Colloidal solutions of Platinum and Palladium were found in some cases to induce rapid reduction even at the ordinary temperature and pressure, the action of a 2 per cent. Platinosol being so energetic that its use as a standard test for unsaturated oils was considered feasible.

When a mixture of Ethylene and Hydrogen is shaken at the ordinary temperature with a stabilised Palladium hydrosol, Ethane is formed rapidly and quantitatively (Paal and Hartmann, *Ber.*, 1909, 42, 2239). Paal and Schwarz obtained similar quantitative results using colloidal Platinum, but the action was not so brisk

(*Ber.*, 1915, 48, 994). Vigorous action ensues under the same conditions with Acetylene, the reaction being much influenced by the rapid adsorption of this gas by all forms of finely-divided or colloidal Platinum or Palladium (Paal and Hohenegger, *Ber.*, 1910, 43, 2684, 2692; 1913, 46, 128; Paal and Schwarz, *Ber.*, 1915, 48, 1195).

The reduction of Acetylene to Ethylene has frequently been attempted. Sabatier and Senderens found that the chief product was always Ethane, even when insufficient Hydrogen for complete reduction to Ethylene was used. Karo (D.R.-P. 253160) claims that by using a catalyst consisting of a Platinum metal diluted with a base metal, the partial reduction of Acetylene to Ethylene can be effected. Paal and Hohenegger, observing that reduction of many Acetylenic derivatives (Phenyl acetylene, Diphenyl diacetylene, Phenyl propiolic acid, etc.) in presence of colloidal Platinum or Palladium enabled intermediate ethylenic compounds to be isolated, attempted the same method with Acetylene. Mixtures of Acetylene and Hydrogen were brought into close contact with a colloidal solution of Palladium both by repeated circulation through the solution and by vigorous agitation. It was found that adsorption of Acetylene by the colloid was so energetic that excess of this constituent in the gas mixture could not be maintained, and that some Ethane was always produced. The highest yield of Ethylene obtained was 70 per cent. of theory (*Ber.*, 1915, 48, 275). The experiments were repeated by Paal and Schwarz, using colloidal Platinum, but the action of Platinum was much slower, and lower yields of Ethylene than 70 per cent. were always obtained (*Ber.*, 1915, 48, 1202).

Paal and Gerum observed that when a solution of Sodium fumarate, $\text{COONa}\cdot\text{CH}:\text{CH}\cdot\text{COONa}$, containing Palladium hydride hydrosol, was exposed to an atmosphere of Hydrogen in a closed vessel, the gas was quickly absorbed and Sodium succinate formed (*Ber.*, 1908, 41, 2273). In the same way, Fumaric and Maleic acids were reduced to Succinic, and Methyl cinnamate and Cinnamic acid, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COOH}$, to Methyl β -phenyl propionate and β -Phenyl propionic acid, respectively. More Hydrogen was absorbed, however, than corresponds with simple reduction of the organic compounds. Palladium-black and colloidal Platinum were shown to be more slowly active.

The hydrogenation of Sodium oleate to stearate at the ordinary temperature in presence of Palladium hydrosol was effected to the extent of 60 per cent. by Paal and Roth (*Ber.*, 1908, 41, 2282). Natural fats, castor oil, cod-liver oil and olive oil were also hydrogenated in the same way, the first two almost completely to hard fats, while olive oil gave a solid which still possessed a low Iodine

value. In a second paper (*Ber.*, 1909, 42, 1541), Paal and Roth extended these observations. By repeating the treatment of oils with colloidal Palladium and Hydrogen in presence of a protective colloid, complete, or very nearly complete, reduction (as estimated by the Iodine value) was obtained. The oils were simply emulsified with water, the hydrosol added, and Hydrogen passed. The rate of reduction was much faster the more perfect the emulsification. The following oils were treated: castor, croton, olive, sesame, cotton-seed, linseed, butter, lard, and oleomargarine from beef fat. In all cases, in attaining complete, or nearly complete reduction, a large excess of Hydrogen was absorbed over that indicated as required by the Iodine value.

Egg-lecithin, a phosphatic fat of Iodine value 55.3, was hydrogenated by Paal and Oehme in 90 per cent. Alcohol solution, using colloidal Palladium. The Hydrolecithin soon began to crystallise out, and on recrystallising from Acetone and Chloroform gave a white powder, sintering at 83–84° C. (*Ber.*, 1913, 46, 1297).

Kelber and Schwarz showed that, using a stabilised Platinum or Palladium hydrosol, acetylenic derivatives could frequently be reduced in stages and the Ethylenic compound isolated (*Ber.*, 1912, 45, 1946). By passing Hydrogen through glacial Acetic acid solutions containing 0.1 gram of colloidal Palladium, Phenyl acetylene, $C_6H_5 \cdot C \equiv CH$, was reduced in a few hours to Styrene, $C_6H_5 \cdot CH : CH_2$, and on longer treatment to Ethyl benzene, $C_6H_5 \cdot C_2H_5$. Tolane, $C_6H_5 \cdot C \equiv C \cdot C_6H_5$, was similarly reduced to Stilbene and isoStilbene, $C_6H_5 \cdot CH : CH \cdot C_6H_5$, and finally to Dibenzyl, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$. Diphenyl diacetylene, $C_6H_5 \cdot C \equiv C : C \equiv C \cdot C_6H_5$, gave first a mixture of the stereoisomeric cis-cis- (25 per cent.) and cis-trans- (75 per cent.) $\alpha\delta$ -Diphenyl- $\Delta^{\alpha\gamma}$ -butadienes, $C_6H_5 \cdot CH : CH \cdot CH : CH \cdot C_6H_5$, the latter of which passed slowly into a third, the trans-trans-stereoisomer on exposure to sunlight. On further reduction these compounds all yielded $\alpha\delta$ -Diphenyl butane.

Paal and Hartmann, by shaking Phenyl propiolic acid, $C_6H_5 \cdot C \equiv C \cdot COOH$, and Palladium hydrosol with Hydrogen until an equimolecular proportion had been absorbed, obtained under different conditions the various stereoisomeric forms of Cinnamic acid, $C_6H_5 \cdot CH : CH \cdot COOH$, especially Allocinnamic acid, showing that cis addition tended more easily to occur (*Ber.*, 1909, 42, 3930). Paal and Schwarz, using colloidal Platinum, also obtained Cinnamic acid nearly free from Phenyl propionic acid, but a lower proportion of the cis-isomer was formed than when colloidal Palladium was used (*Ber.*, 1918, 51, 640). Further reduction of either form of Cinnamic acid yielded β -Phenyl propionic acid (Paal and Gerum, *Ber.*, 1908, 41, 2273).

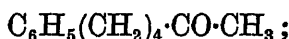
Williams and James (*Chem. Abs.*, 1923, 3493), reducing Tetrollic

acid in the same way, found again that *cis* addition occurred more readily, a 63 per cent. yield of Allocrotonic acid and only a 4 per cent. yield of ordinary Crotonic acid being obtained. Reduction of Acetylene dicarboxylic acid, $\text{COOH}\cdot\text{C}:\text{C}\cdot\text{COOH}$, on the other hand, gave no Maleic acid at all, but only Fumaric, formed by *trans* addition, which, however, further reduced very rapidly to Succinic acid.

Experiments on the selective hydrogenation of Ethylenic groups, where two or more are present in the same molecule, were carried out by Paal. He concluded that only those compounds in which the two unsaturated groups are separated by at least one saturated Carbon atom are capable of partial reduction. Thus, using colloidal Palladium as catalyst and absorbing half the volume of Hydrogen requisite for complete reduction, in the following cases the product consisted of approximately 50 per cent. of unchanged initial substance and 50 per cent. of the completely reduced derivative. The hydrogenation was carried out in Alcohol solution at 2 atmospheres pressure of Hydrogen. Cinnamylidene methyl ketone,



gave unchanged ketone and δ -Phenyl-butyl methyl ketone,



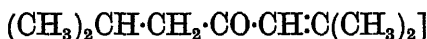
and Sodium cinnamylidene malonate, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{C}(\text{COONa})_2$, Piperic acid, and Piperine treated in the same way gave only the completely reduced tetrahydro-derivatives. On the other hand, Phorone,



and Dibenzylidene acetone (Distyryl ketone,



in which the unsaturated groups were further separated, gave in each case, first, the partially reduced derivatives isoButyl isobutenyl ketone [Dihydrophorone,



and Phenyl-ethyl styryl ketone, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_5$, which could be isolated in good yields, and, secondly, on further reduction, the completely hydrogenated substances Valerone,

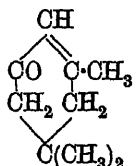


and Dibenzyl acetone, $(\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{CO}$ (Paal, *Ber.*, 1912, 45, 2221).

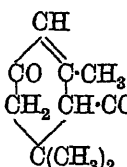
The great value of Paal's method is in the possibility of graduated reduction. The conditions under which, when two unsaturated

groups are present, they can be separately reduced, have been indicated. Wallach (*Ann.*, 1911, 381, 51), Paal (*loc. cit.*, and D.R.-P. 298193), and Skita have shown that ethylenic groups can be reduced almost quantitatively in whatever position, whether part of a ring or an open chain, and that in the case of unsaturated aldehydes and ketones this can be effected before the carbonyl group commences to be attacked, while alcoholic, methoxy, and carboxylic acid groups are stable under all conditions. In the terpene group these advantages are very considerable, and, according to Wallach, for such compounds Paal's method is the most valuable means of reduction known.

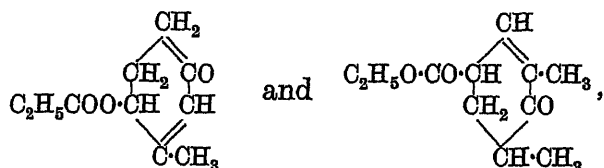
Cyclic ketones, unsaturated in the $\alpha\beta$ -position, with mild reducers generally give more or less dicyclic ketone along with the normal saturated product, while stronger agents attack both unsaturated and carbonyl groups, and usually effect bye-reactions in addition. These complications are avoided by dissolving the unsaturated cyclic ketone in Alcohol, adding an aqueous solution of Palladious chloride and gum arabic, and shaking in an atmosphere of Hydrogen. The unsaturated linkage is reduced completely before the carbonyl

group is affected. Thus, isoPhorone,  in 2 hours

is reduced to an 82 per cent. yield of Dihydroisophorone. Ethyl isophorone carboxylate (Ethyl 1:1:3-trimethyl-3-cyclohexene-5-

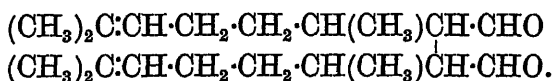
one-2-carboxylate), , gives the two stereoisomeric

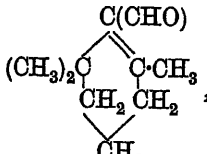
modifications of Dihydroisophorone carboxylic ester. In the same way, 1-Methyl- Δ^1 -cyclohexen-3-one-6-carboxylic ethyl ester, and 1:3-Dimethyl- Δ^3 -cyclohexenone-5-carboxylic ethyl ester,



give high yields of the corresponding Cyclohexanone carboxylic esters.

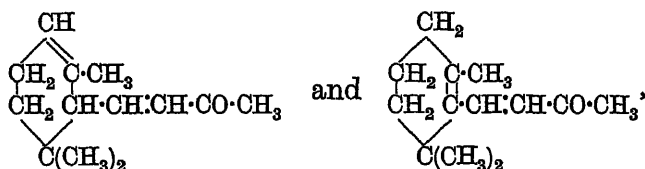
Enklaar (*Ber.*, 1908, 41, 2083) found that the $\alpha\beta$ -unsaturated aldehyde Citral, $(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3):\text{CH}\cdot\text{CHO}$, when subjected to Sabatier and Senderens' method of hydrogenation, gave a series of cyclic compounds. With colloidal Palladium and Hydrogen, on the other hand, two atoms of Hydrogen were first added, with formation of the aldehyde Citronellal and the alcohol Citronellol, together with an oil, probably the bimolecular aldehyde,



β -Cyclocitral, also an $\alpha\beta$ -unsaturated aldehyde, 

in the same way reduced to 2 : 2 : 6-Trimethyl hexahydrobenzaldehyde (Skita, *Ber.*, 1909, 42, 1627).

The physiological properties of substances may be much modified by hydrogenation. For example, α - and β -Ionones,



easily add two atoms of Hydrogen, giving two different Dihydro-ionones, both of which possess odours very distinct from that of Ionone. Further reduction of these dihydro-bodies gives the same Tetrahydroionone. Since reduction in the ring would yield identical Dihydroionones, it would appear that the side-chain is first reduced. Tiemann's view, that the characteristic perfume of Ionone is conferred by the unsaturated ketonic side-chain, is also confirmed. Both conclusions were established by Skita and Meyer's synthesis from Dihydro-cyclocitral, of the Dihydroionone saturated in the nucleus, but unsaturated in the side-chain, which possesses the characteristic perfume of Ionone.

Many alkaloids have been hydrogenated, yielding hydro-derivatives possessing, in some cases, distinct physiological properties, as, for example, Dihydromorphine, the effects of which are more lasting than those of Morphine, and Tetrahydrocolchicine, which is less toxic than Colchicine.

The following alkaloids have been hydrogenated, the conditions

of reaction and the corresponding products being indicated in the table:—

| Alkaloid. Conditions of reaction. | Product. | References. |
|--|--|---|
| Strychnine, Acid solution, Pd, and gum arabic. Hydrogen 2 atm. | Dihydrostrychnine, $C_{21}H_{24}O_2N$. | D.R.-P. 230724. |
| Strychnine, same conditions. Hydrogen 3 atm. | Tetrahydrostrychnine, $C_{21}H_{26}O_2N$. | |
| Brucine, same conditions. Hydrogen 2 atm. | Dihydrobrucine, $C_{23}H_{28}O_4N_2$. | D.R.-P. 260233 |
| Morphine hydrochloride, Pd, and gum arabic. | Dihydromorphine, $C_{17}H_{21}O_3N$. | |
| Codeine hydrochloride, Pd, and gum arabic. | Dihydrocodeine, $C_{18}H_{23}O_3N$. | E.P. 3948 of 1912 |
| Quinine hydrochloride, Pd, and gum arabic. | Dihydroquinine, $C_{20}H_{26}O_2N_2$. | |
| Cinchonine hydrochloride, Pd, and gum arabic. | Dihydrocinchonine, $C_{19}H_{24}ON_2$. | U.S.P. 989664. |
| Piperine hydrochloride, Pd, and gum arabic. | Tetrahydropiperine, $C_{17}H_{23}O_3N$. | Borsche, <i>Ber.</i> , 1901, 44, 2942. Paal, <i>Ber.</i> , 1912, 45, 2221. |
| Colchicine: Colloidal Pt. | Tetrahydrocolchicine, $C_{22}H_{28}O_6N$. | D.R.-P. 279999. |
| Quinidine: Colloidal Pd; no protective colloid. | Dihydroquinidine, $C_{20}H_{26}O_2N_2 \cdot H_2O$ (identical with natural Hydrocon- quinine) | Skita and Nord, <i>Ber.</i> , 1912, 45, 3312. |
| Cinchonidine: Colloidal Pd; no protective colloid. | Dihydrocinchonidine, $C_{19}H_{24}ON_2$. | |
| Diacetyl morphine: Colloidal Pd; no protective colloid. | Diacetyl dihydro- morphine. | Skita and Meyer, <i>Ber.</i> , 1912, 45, 3579. |

Skita and Frank, *Ber.*, 1911, 44, 2862.

The following unsaturated compounds also have been reduced by Paal's method: Mesityl oxide and Phorone (Wallach, *Nachr. Gess. der Wiss. Göttingen*, 1910, 517; Skita, *Ber.*, 1909, 42, 1627). 1:10-Diphenyl-1:9-decadiene, $C_6H_5 \cdot CH:CH(CH_2)_6 \cdot CH:CH \cdot C_6H_5$ (Borsche and Wollemann, *Ber.*, 1911, 44, 3185). Carvone and Pinene (Paal, *Ber.*, 1912, 45, 2221; Skita and Meyer, *Ber.*, 1912, 45, 3579). Citral, in two stages to Citronellal and Dihydrocitronellal, Geraniol to Citronellol and Dihydrocitronellol; Linalool to dihydro- and tetrahydro-derivatives, and Geranic acid to the dihydro-(*r*-Citronellic) and tetrahydro-acids (Paal, D.R.-P. 298193 of 1913). *d*- and *l*- α -Terpineol, β -Terpineol, Sylveterpineol, Pinol hydrate, Pineol, *d*-Carvone, Eucarvone, α -Dicarvelone, Carvenolide, Pulegenolide, Pulegenamide, α -Fenchonenitrile, β -Fencholenamide, Campholenonitrile, Thuja ketone; Thuja ketonic acid, Tanacetophorone, isoThujone, Methyl heptenone; Δ^1 - and Δ^3 -Tetrahydro-*p*-acetyl toluene; the Cyclohexene and Methyl cyclohexene acetic acids (Wallach, *Ann.*, 1911, 381, 51). α - and β -Caryophyllenes and β -Caryophyllene

nitrosite (Deussen and Vielitz, *Ann.*, 1912, 388, 136). Artemisin, $C_{15}H_{20}O_4$ (Rimini and Jona, *Rend. Soc. Chim. Ital.*, (2), 5, 52).

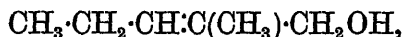
Aldehydes and Ketones

Aldehydes and ketones can be reduced by Hydrogen in presence of colloidal Platinum or Palladium, but usually only slowly, or not at all under the mild conditions which are sufficient to hydrogenate completely any unsaturated groups present in the same molecule. Thus, Wallach found that unsaturated groups in open chain, or hydroaromatic substances of the terpene group—whether they formed part of a side-chain or ring, could be reduced almost quantitatively without attack upon any aldehydic or ketonic group present (*Ann.*, 1911, 381, 51).

Skita and Meyer found that in some cases, especially among the $\alpha\beta$ -unsaturated aldehydes, a certain amount of reduction of the carbonyl group occurred simultaneously with the hydrogenation of the unsaturated group, the relative proportions of the double bond and carbonyl group attacked depending upon the respective reaction velocities. The ethylenic linkage was always reduced much more rapidly than the carbonyl group, and more noticeably was this the case with unsaturated ketones. Hence, while the product of reduction of an unsaturated aldehyde or ketone was almost entirely the corresponding saturated aldehyde or ketone, in some cases, and more often with aldehydes, a small quantity of alcohol was formed (*Ber.*, 1909, 42, 1627; 1912, 45, 3312). Thus, α -Methyl β -ethyl acraldehyde in aqueous alcoholic solution

(19.4 grams of aldehyde in 50 c.c. of Alcohol, 20 c.c. of water, with 20 c.c. of 1 per cent. $PdCl_2$, 20 c.c. of 2 per cent. gum arabic, and Hydrogen at 2 atmospheres pressure)

at ordinary temperatures absorbed 1 molecular equivalent of Hydrogen, giving a mixture of α -Methyl n -valeric aldehyde, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CHO$, and β -Methyl pentenyl alcohol,



in the proportions of 9 to 1. A strange feature of this reaction is that the small proportion of unsaturated alcohol formed cannot be further reduced even when the Hydrogen pressure is increased to 3 atmospheres, in spite of the fact that, under the same conditions, Allyl alcohol, $CH_2 : CH \cdot CH_2OH$, Propyl allyl alcohol,



as well as Acraldehyde, $CH_2 : CH \cdot CHO$, are readily reduced to saturated substances. In Acetic acid solution the reduction of α -Methyl β -ethyl acraldehyde is normal, 1 molecular equivalent of Hydrogen

being rapidly absorbed, followed by the slower absorption of a second, giving the Hexyl alcohol, $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{OH}$.

The more vigorous hydrogenating conditions employed by Skita and Meyer for reduction of the aromatic nucleus were then shown to effect the reduction of Heptaldehyde to Heptyl alcohol, and Dihydro isophorone to Dihydro isophorol (*Ber.*, 1912, 45, 3589), and still more recently Skita and Stuckart have generalised the method (*Ber.*, 1915, 48, 1486). Using Hydrogen at a small additional pressure, aqueous Acetic acid as solvent, colloidal Platinum as catalyst, and prolonging the action until the requisite quantity of Hydrogen was absorbed, many aldehydes and ketones were reduced, the aliphatic giving the corresponding primary or secondary alcohols, while the aromatic tended to reduce completely to hydrocarbons, the intermediate alcohol being isolable only in certain instances by carefully regulated control. It was noticed that reduction *in situ* of a solution of Platinic chloride, or Chloroplatinic acid in presence of gum arabic and a small quantity of inoculation colloid, often yielded a more active catalyst than when a colloidal solution, already prepared, was added to the reaction mixture. Regulation of the reaction was effected by variation of the solvent, the Hydrogen pressure, the temperature, and the concentration of the catalyst, as follows: In aqueous alcoholic solution, the aldehydic or ketonic group was only slowly reduced, or not at all. In Acetic acid solution, on the other hand, aliphatic aldehydes and ketones gave easily the corresponding alcohols, while aromatic aldehydes and ketones reduced more completely, hydrocarbons only being obtainable. In those cases where aromatic alcohols were obtained by reduction of the corresponding carbonyl compound, the necessary vigour of reduction was obtained by raising the temperature, amount of catalyst, and Hydrogen pressure, while using a milder solvent.

Acetone

(5 grams in 40 c.c. of Acetic acid, with 10 c.c. of 5 per cent. H_2PtCl_6 , 25 c.c. of gum arabic, 10 c.c. of colloidal Platinum, and Hydrogen at 4 atm.)

absorbed 1 molecular equivalent of Hydrogen in 30 hours, giving a quantitative yield of isoPropyl alcohol. The same conditions effected the quantitative reduction in 2 hours of Methyl propyl ketone, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$, and Diethyl ketone, $\text{C}_2\text{H}_5 \cdot \text{CO} \cdot \text{C}_2\text{H}_5$. Cyclohexanone in the same way reduced in 40 minutes to Cyclohexanol with a little Cyclohexane. In alcoholic solution these reductions required a much longer time. Acetyl acetone, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$, under similar conditions absorbed 3 molecular equivalents of Hydrogen in 4 hours, and gave Methyl propyl carbinol, $\text{CH}_3 \cdot \text{CHOH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$. Phenyl acetaldehyde, $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CHO}$

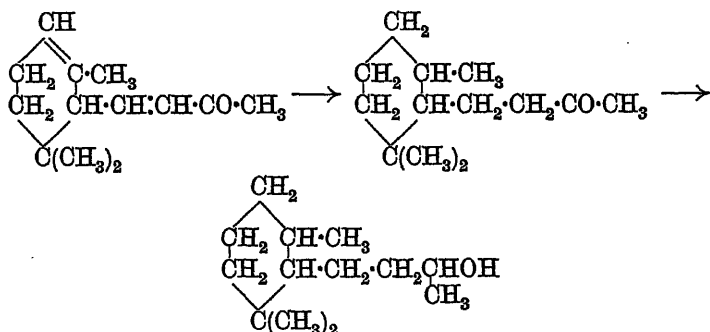
(6.8 grams in 25 c.c. of Acetic acid, with 10 c.c. of 5 per cent. H_2PtCl_6 , 20 c.c. of gum arabic, and 10 c.c. of colloidal Platinum)

absorbed 1 molecular equivalent of Hydrogen in 4 hours, and gave Phenyl ethyl alcohol with a small quantity of Ethyl benzene.

α - and β -Ionones

(10 grams in 50 c.c. of Acetic acid, with 10 c.c. of 5 per cent. H_2PtCl_6 , 20 c.c. of gum arabic, and 10 c.c. of colloidal Platinum)

were reduced to Tetrahydro ionone in 40 minutes, and to 1:1:3-Trimethyl-2- γ -hydroxybutyl cyclohexane in 4 hours:—



Pulegone similarly was reduced first to the dihydro-body, and then to Menthol.

Mesityl oxide, $(\text{CH}_3)_2\text{C}:\text{CH}:\text{CO}:\text{CH}_3$, was easily reduced to iso-Butyl methyl ketone, $(\text{CH}_3)_2\text{CH}:\text{CH}_2:\text{CO}:\text{CH}_3$

(5 grams of Mesityl oxide in 20 c.c. of water, with 10 c.c. of colloidal Platinum = 0.031 gram, Hydrogen 2 atm.)

or to isoButyl methyl carbinol, $(\text{CH}_3)_2\text{CH}:\text{CH}_2:\text{CHOH}:\text{CH}_3$

(5 grams Mesityl oxide in 40 c.c. of Acetic acid, with 10 c.c. of 5 per cent. H_2PtCl_6 , 25 c.c. of gum arabic, and 10 c.c. of inoculation colloid = 0.24 gram Pt.).

Aromatic aldehydes and ketones can sometimes, under mild conditions, be reduced to alcohols: thus Benzaldehyde

(5 grams in 35 c.c. of Alcohol, with 25 c.c. of colloidal Platinum solution = 0.08 gram Pt, 10 c.c. of water, Hydrogen at 2 atm.)

absorbs 1 molecular equivalent of Hydrogen in 5 hours, giving Benzyl alcohol. In Acetic acid solution, the reduction does not stop at the alcohol stage, Benzaldehyde

(5 grams in 45 c.c. of Acetic acid, with 5 c.c. of 5 per cent. H_2PtCl_6 , 12.5 c.c. of 2 per cent. gum arabic, and 5 c.c. of inoculation colloid = total Pt content of 0.12 gram, and Hydrogen at 2 atm.)

absorbing 1 molecular equivalent of Hydrogen in 1 hour and 2 in 10 hours, forming 4 grams of Toluene. Yet more energetic conditions

(5 grams Benzaldehyde in 50 c.c. of Acetic acid, with 10 c.c. of 5 per cent. H_2PtCl_6 , 15 c.c. of gum arabic, 8 c.c. of inoculation colloid, and Hydrogen at 3 atm.)

result in the absorption of 5 molecular equivalents of Hydrogen in 10 hours, with formation of Methyl cyclohexane.

Benzophenone is similar, but the reduction cannot be moderated to yield the secondary alcohol. In Acetic acid solution

(10 grams of Benzophenone, in 200 c.c. of Acetic acid, with 20 c.c. of 5 per cent. H_2PtCl_6 , 15 c.c. of inoculation colloid, and 45 c.c. of gum arabic in 50 c.c. of water; temperature 60°C .)

8 molecular equivalents of Hydrogen are absorbed in $1\frac{1}{2}$ hours, forming Dicyclohexyl methane, $(\text{C}_6\text{H}_{11})_2\text{CH}_2$.

The graduated reduction possible by the use of colloidal catalysts is further illustrated by the hydrogenation of Cinnamaldehyde. In aqueous-alcoholic solution, only the ethylenic linkage is reduced; thus,

10 grams of aldehyde in 100 c.c. of Alcohol, with 10 c.c. of 1 per cent. PdCl_2 and 20 c.c. of 2 per cent. gum arabic in 30 c.c. of water,

absorbs 1 molecular equivalent of Hydrogen in about 1 hour, after which the colloid flocculates and absorption of Hydrogen ceases. The product is Phenyl propionaldehyde, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO}$, with a small quantity of Cinnamyl alcohol, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\text{OH}$. In Acetic acid solution, with a Platinum catalyst formed from Platinic chloride during the reaction, the aldehyde group is reduced. Thus

6 grams of aldehyde in 45 c.c. of Acetic acid, with 10 c.c. of 5 per cent. H_2PtCl_6 , 25 c.c. of 2 per cent. gum arabic, 10 c.c. of inoculation colloid, and Hydrogen at 2 atmospheres

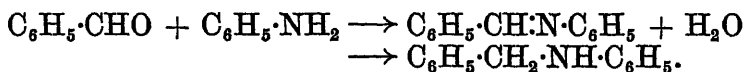
absorbs 1 molecular equivalent of Hydrogen in $\frac{1}{2}$ hour, and 2 in 6 hours, after which no further absorption occurs even on raising the Hydrogen pressure to 4 atmospheres. The product is mainly Phenyl propyl alcohol, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$, with a small quantity of Phenyl propane. Increased concentration of catalyst and a higher Hydrogen pressure effect hydrogenation of the aromatic ring. Thus

5 grams of aldehyde in 50 c.c. of Acetic acid, with 10 c.c. of 10 per cent. H_2PtCl_6 , 30 c.c. of 2 per cent. gum arabic, 16 c.c. of inoculation solution, and Hydrogen at 4 atmospheres

absorb Hydrogen corresponding to the first reduction stage in $\frac{1}{2}$ hour, reaches the second stage in $1\frac{1}{2}$ hours, and the third stage, where 5 molecular equivalents of Hydrogen are absorbed, in 5 hours. The chief product is Cyclohexyl propyl alcohol, $\text{C}_6\text{H}_{11}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$, but small quantities of Propyl benzene, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$, and Propyl cyclohexane, $\text{C}_6\text{H}_{11}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$, suggest that the reduction follows in part the course common with aromatic aldehydes and ketones.

Attempts were made to protect the carbonyl group in aromatic aldehydes and ketones in such a way that hydrogenation would yield the corresponding hydroaromatic aldehydes or ketones (Skita and Brunner, *Ber.*, 1915, 48, 1685). Some protection appeared to be afforded by masking the aldehydic group by acylation, since Phenyl acetaldehyde, $C_6H_5 \cdot CH_2 \cdot CHO$, reduced more easily, and gave a higher yield of Phenyl ethyl alcohol when used in the enolic form of its acetic ester, Phenyl vinyl acetate, $C_6H_5 \cdot CH:CH \cdot O \cdot CO \cdot CH_3$. This was not a general method of protection, however, since Benzyl acetate, Benzyl benzoate, and Benzylidene diacetate were reduced, like Benzaldehyde and Benzyl alcohol, to Toluene. That the vigour of hydrolysis which accompanies hydrogenation is very great is illustrated by the fact that Benzyl ethyl ether, $C_6H_5 \cdot CH_2 \cdot O \cdot C_2H_5$, also is reduced to Toluene.

After condensation with Aniline the reduction of aromatic aldehydes and ketones to the corresponding cyclohexyl bodies was possible. Thus, Benzaldehyde was condensed with Aniline and the Benzylidene aniline so formed reduced with Sodium and Alcohol to Benzyl aniline :

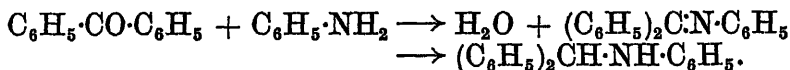


This was hydrogenated in presence of colloidal Platinum

(15 grams of base in 150 c.c. Acetic acid, with 60 c.c. of 10 per cent. H_2PtCl_6 , 22 c.c. 10 per cent. gum arabic, 15 c.c. of inoculation colloid, and Hydrogen at 4 atm.)

when 6 molecules of Hydrogen were absorbed in 3 hours. The product of reduction was rendered alkaline, and extracted with ether (or steam distilled), whereby Cyclohexyl cyclohexyl-methyl amine, $C_6H_{11} \cdot CH_2 \cdot NH \cdot C_6H_{11}$, was obtained, together with smaller quantities of Cyclohexylamine and Methyl cyclohexane. Simultaneous oxidation and hydrolysis of the base by means of Potassium permanganate in aqueous acetone solution gave Hexahydrobenzaldehyde, $C_6H_{11} \cdot CHO$, identical with the compound previously synthesised by Wallach.

Benzophenone was condensed with Aniline, and the Diphenyl methylene aniline so formed reduced with Sodium and Alcohol to Diphenylmethyl aniline,



In presence of Platinum, this base

(5 grams in 113 c.c. of Acetic acid, with 35 c.c. of 10 per cent. H_2PtCl_6 , 17 c.c. of inoculation colloid, 10 c.c. of gum arabic, 75 c.c. of water, and 100 c.c. of Acetic acid; temperature $50^\circ C$. and Hydrogen pressure 2 atm.)

absorbed 3 molecules of Hydrogen in 5 minutes and 6 molecules in 20 minutes, giving a mixture of Cyclohexylamine, Dicyclohexyl methane, $(C_6H_{11})_2CH_2$, but chiefly Cyclohexylaminocyclohexyl phenyl methane, $\begin{matrix} C_6H_{11} \\ C_6H_5 \end{matrix} > CH \cdot NH \cdot C_6H_{11}$. Simultaneous oxidation and hydrolysis of this base with Chromic acid gave Cyclohexyl phenyl ketone, $C_6H_{11} \cdot CO \cdot C_6H_5$, characterised by its oxime and semi-carbazone.

Hydrogenation of Aromatic Substances

According to Sabatier, "La Catalyse en Chimie Organique," 1913, 120, colloidal metals are unable to effect hydrogenation of the aromatic nucleus. The powerful influence of the solvent on the rate of hydrogenation in solution, observed by Fokin, was, however, turned to account by Willstätter and Hatt (*Ber.*, 1912, 45, 1471), who showed that Acetic acid in particular promoted hydrogenation, and in contact with Platinum-black enabled the aromatic nucleus to be hydrogenated. Skita and Meyer extended this discovery to the case of colloidal metals, and showed that, whereas aromatic substances could seldom be hydrogenated in contact with colloidal Platinum in media other than Acetic acid, when this solvent was used, together with a sufficient concentration of catalyst and pressure of Hydrogen, complete hydrogenation occurred, even in cases where the Sabatier and Senderens method yielded only incompletely hydrogenated products (*Ber.*, 1912, 45, 3589). The catalyst used consisted of colloidal Platinum, formed during the reaction by adding a chloride of Platinum to the reaction mixture dissolved in Acetic acid together with gum arabic and a small quantity of inoculation solution to cause separation of the reduced Platinum in the colloidal form. Hydrogen was used at a pressure of 1 atmosphere excess over atmospheric.

Benzene and Toluene gave Cyclohexane and Methyl cyclohexane, respectively. Naphthalene was hydrogenated in two stages to Tetrahydro- and Decahydro-naphthalene, while Pyridine and Benzoic acid, which cannot be hydrogenated by the Sabatier and Senderens method, gave readily Piperidine and Cyclohexane carboxylic acid, respectively, within 1 to 3 hours.

Heterocyclic compounds were similarly hydrogenated, but often required longer treatment and a higher Hydrogen pressure. Thus, Quinoline was reduced to Tetrahydroquinoline, and on more prolonged treatment to Decahydroquinoline.

A later paper described the reduction of homologues of Pyridine and of alkaloid derivatives of Quinoline (Skita and Brunner, *Ber.*, 1916, 49, 1597). In these cases the colloidal solution was prepared immediately before use by reduction of Platinic chloride in presence of gum arabic, and the substance to be hydrogenated, dissolved in

Acetic acid, added afterwards. The presence of Acetic acid was preferable in all cases except that of Pyridine, which reduced more rapidly in dilute Hydrochloric acid. Substances must be pure for satisfactory hydrogenation; a condition best obtained in the case of bases by recrystallation of their picrates.

Pyridine

(3 grams added to 0.7 gram of gum arabic, 0.26 gram of colloidal Platinum in 86 c.c. of water, and 5 c.c. of strong Hydrochloric acid. Hydrogen pressure 3.5 atm., temperature 20° C.)

absorbed 3 litres of Hydrogen in 50 minutes, giving Piperidine, with a small amount of Pentane.

Homologues of Pyridine reduced more slowly. Pure α -Picoline

(3 grams in 50 c.c. of Acetic acid, added to a solution made by shaking with Hydrogen 5 c.c. of 10 per cent. H_2PtCl_6 , 6 c.c. of 10 per cent. gum arabic, 4 c.c. of inoculation colloid, and 35 c.c. of water)

at 25° C. and 4 atmospheres pressure of Hydrogen, absorbed 2.4 litres in $3\frac{1}{2}$ hours, giving α -Pipicoline.

$\alpha\gamma$ -Lutidine reduced still more slowly, and required 9 hours under the same conditions, but at 45° C. gave $\alpha\gamma$ -Lupetidine in $1\frac{3}{4}$ hours. 2 : 4 : 5-Collidine similarly gave 2 : 4 : 5-Copellidine.

Atophan (1 Phenyl quinoline-3-carboxylic acid)

(5 grams in 210 c.c. of Acetic acid, added to 5 c.c. of reduced 10 per cent. H_2PtCl_6 , 28 c.c. of 10 per cent. gum arabic, 17 c.c. of inoculation colloid, and 90 c.c. water, Hydrogen at 2 atm., and temperature 59° C.)

absorbed 2 molecules of Hydrogen in 40 minutes, giving Tetrahydro atophan (1-Phenyl 1 : 2 : 3 : 4-tetrahydro quinoline-3-carboxylic acid). Stronger conditions

(10 c.c. of 10 per cent. H_2PtCl_6 , Hydrogen at 4 atm., and temperature 52° C.)

effected absorption of 5 molecules of Hydrogen in 50 minutes, with formation of Decahydro atophan.

Dihydroquinine

(2.16 grams in 20 c.c. of Acetic acid added to a reduced solution of 23 c.c. of 10 per cent. H_2PtCl_6 , 4 c.c. of inoculation colloid, and 6 c.c. of 10 per cent. gum arabic in 28 c.c. of Acetic acid, Hydrogen 3 atm. temperature 45° C.)

reduced in 1 hour to Hexahydrocinchonidine. More vigorous conditions

(3.26 grams in 20 c.c. of Acetic acid added to a reduced solution of 12 c.c. of 20 per cent. H_2PtCl_6 , 4 c.c. of inoculation solution, 3.6 grams of gum arabic in 19 c.c. of water and 30 c.c. of Acetic acid, Hydrogen at 4 atm.)

gave in 4 hours at 48° C. Decahydro cinchonidine.

Dihydro cinchonidine reduced similarly in two stages to the same two products. Cinchonine under similar conditions hydrogenated to

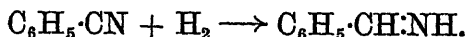
Hexahydro cinchonine, and anhydrous Dihydro quinidine to a mixture of Hexahydro cinchonine and a compound of the formula $C_{20}H_{30}ON_2, H_2O$.

Gum arabic was the only satisfactory protective colloid for reduction of aromatic and heterocyclic substances.

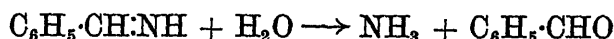
Nitriles and Oximes

Benzonitrile, $C_6H_5 \cdot CN$, in aqueous-alcoholic solution is reduced at the ordinary temperature by Hydrogen and colloidal Palladium, giving a mixture of Benzylamine, $C_6H_5 \cdot CH_2 \cdot NH_2$; Dibenzylamine, $(C_6H_5 \cdot CH_2)_2NH$, Ammonia, and a little Benzaldehyde (Paal and Gerum, *Ber.*, 1909, 42, 1553).

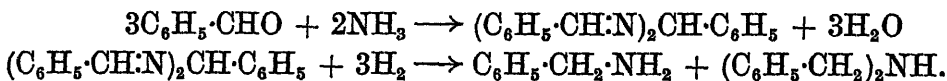
Benzylidene-imine was supposed to be the first product of reduction, although attempts to isolate it were unsuccessful,



Benzaldehyde and Ammonia were then formed by hydrolysis:



and the amines as follows:



Palladium-black behaved similarly but less rapidly, giving the same products, except that the Benzaldehyde was reduced to Benzyl alcohol.

Mandelonitrile (Benzaldehyde cyanhydrin), $C_6H_5 \cdot CHOH \cdot CN$, gave Benzylamine, Dibenzylamine, Benzyl alcohol, and Ammonia when treated in the same way. Partial hydrolysis of the hydroxy nitrile in aqueous-alcoholic solution to Benzaldehyde and Hydrocyanic acid was assumed, the latter being then reduced to Ammonia. Interaction between Benzaldehyde and Ammonia to form Hydrazo-benzamide then followed, as in the case of Benzonitrile, and the amines were formed from this as before, by reduction. The Benzyl alcohol was formed by reduction of some of the aldehyde.

Benzaldoxime, $C_6H_5 \cdot CH:NOH$, gave the same product as Benzonitrile, and the same reaction mechanism was suggested, either direct reduction to Benzylidene imine, which then, by hydrolysis and reduction, behaved as before, or the oxime was first hydrated to Benzaldehyde and Hydroxylamine, the latter reduced to Ammonia, the aldehyde and Ammonia then combining and undergoing reduction to the amines.

Inorganic Reductions

Paal, Hartmann, and Brünjes reduced oxides and hydroxides of heavy metals by adding colloidal Palladium, stabilised with Sodium protalbate, and agitating the suspensions with Hydrogen at the ordinary or slightly elevated temperature (*Ber.*, 1914, 47, 2202).

Cupric hydroxide, either colloidal or precipitated, was reduced to a solution of colloidal Copper. Colloidal Cuprous oxide was in some instances formed intermediately. Precipitated or colloidal Nickel hydroxide similarly gave a solution of colloidal Nickel. Ammonium chromate in the same way reduced to a colloidal solution of Chromic hydroxide, Ammonium metavanadate to colloidal Vanadium trihydroxide, and Ammonium molybdate to colloidal Molybdenum tetrahydroxide. Paal and Büttner showed later that Molybdenum tetrahydroxide, the product of reduction at the ordinary temperature, recommenced to absorb Hydrogen if the temperature was raised to 50–60° C., and the trihydroxide was formed as a dark sludge (*Ber.*, 1915, 48, 220).

Union of Hydrogen and Oxygen. When mixtures of Hydrogen and Oxygen in theoretical proportions were shaken with colloidal Platinum solution, protected by Sodium protalbate, the two gases combined at a rate depending upon the concentration of the catalyst. Direct proportionality between the reaction velocity and the concentration of the colloidal Platinum could not, however, be obtained, either when the reacting substances were well agitated or when the reaction was allowed to proceed at rest. When the reaction was carried out in a gas burette over Mercury, the action quickly slackened, and finally stopped, owing to the poisonous action of the Mercury (Paal and Schwarz, *J. pr. Chem.*, 1916, ii, 93, 106).

Paal and Hartmann showed that when colloidal Platinum was the catalyst the reaction velocity between Hydrogen and Oxygen was a maximum when the gases were present in theoretical proportions. Using colloidal Palladium, on the other hand, excess of Hydrogen over the theoretical proportion increased, and excess of Oxygen decreased the reaction velocity; a difference in behaviour attributed to the much superior affinity of Palladium for Hydrogen (*J. pr. Chem.*, 1909, ii, 80, 337).

The union of Carbon monoxide and Oxygen is likewise promoted by colloidal metals of the Platinum group. Wieland showed that Carbon monoxide was oxidised to Carbon dioxide at the ordinary temperature by Palladium-black in the presence of moisture. This occurred even in the absence of free Oxygen, and was proved to be due to the intermediate formation of Formic acid (*Ber.*, 1912, 45, 679).

Paal showed that Carbon monoxide and Oxygen remained un-

changed in contact with Platinum-black whether water was present or not. Using colloidal Platinum containing Sodium protalbate, however, the Carbon monoxide was slowly oxidised to Carbon dioxide. With colloidal Iridium, formation of Carbon dioxide was rather slower, and with colloidal Osmium very slow, the Osmium gradually oxidising, giving the tetroxide, which exerted but a feeble action (*Ber.*, 1916, 49, 548).

Researches of Willstätter

Fokin, in the researches which we have already mentioned, discovered the hydrogenating properties towards organic substances in liquid media possessed by Platinum and Palladium in either the finely-divided or colloidal forms. He showed that when certain unsaturated substances were dissolved in Ether, Platinum or Palladium-black added, and a current of Hydrogen passed at the ordinary temperature, complete hydrogenation was effected. This method was extended by Willstätter and his collaborators to almost universal application. Platinum and Palladium-black were prepared by Willstätter by the method of Loew, described in the preceding chapter.

Recently Willstätter has obtained improved results in Loew's method by using caustic Potash instead of caustic Soda. The sparingly soluble Potassium platonic chloride, K_2PtCl_6 , separates out, so that reduction is slower, and rise of temperature, formation of a Platinum mirror, and foaming are more easily avoided, resulting in a smoother reduction and a better product (Willstätter and Waldschmidt-Leitz, *Ber.*, 1921, 54 B, 113). Twenty grams of Platinum are dissolved to 80 c.c. of a Hydrochloric acid solution of Chloroplatinic acid, and 150 c.c. of 33 per cent. Formaldehyde solution at $-10^\circ C.$ then added. The solution is kept cool and stirred vigorously while 420 grams of 50 per cent. caustic Potash are added, drop by drop, at a temperature not higher than $4-6^\circ C.$ The solution is then warmed to $55-60^\circ C.$ for $\frac{1}{2}$ hour, after which the precipitate is washed by decantation until free from chloride and alkali, carefully keeping the Platinum immersed in the liquid. Finally the precipitate is quickly pressed, and evacuated at a good pump. After about 2 days its weight becomes constant, and it ceases to form water on storing in a closed bottle. As made in this way, the metal is almost free from Oxygen, which it adsorbs with avidity, forming a highly active catalyst which is stable indefinitely.

Palladium-black can be made in the same way. Willstätter prepared it from Palladious chloride by dissolving a quantity containing 4.25 grams of Palladium to 100-150 c.c. in dilute Hydrochloric acid, adding 50 c.c. of 33 per cent. Formaldehyde, and cooling to $0-3^\circ C.$ while 100 grams of 50 per cent. caustic Potash

solution were run in during 10 minutes. The reaction was then completed by warming for 15 minutes at 60° C., and the Palladium-black collected in the way described for Platinum.

According to Liebig, Platinum-black is capable of absorbing 800 times its volume of Oxygen. The "black" prepared by Mond, Ramsay, and Shields (*Proc. R.S.*, 1895, 58, 242) was stated to contain 100 volumes of occluded Oxygen, and when brought into the presence of Hydrogen absorbed 310 volumes of this gas, 200 of which were eventually used in combining with the Oxygen. It was shown by Mond, Ramsay, and Shields (*Proc. R.S.*, 1897, 62, 50), and confirmed by Willstätter, that adsorbed Hydrogen and Oxygen can co-exist as such in Platinum-black, and the former investigators assumed a combination to Platinous hydroxide. This was supported by the evidence that the heat of formation of Platinous hydroxide is approximately equal to the heat of adsorption of Oxygen by Platinum-black, and by the fact that Platinum-black containing Oxygen gives many reactions in common with Platinous hydroxide, such as the liberation of Iodine from Potassium iodide and the oxidation of Arsenious acid to Arsenic. Adsorption of Oxygen and Hydrogen, probably in monatomic form, by primary valence forces suffices, however, to explain these phenomena, and accounts for the powerful catalytic action, both oxidising and hydrogenating, of finely-divided Platinum. Certainly the Hydrogen which Platinum or Palladium takes up when in an active catalytic state is more easily dissociable and more reactive than in Platinum or Palladium hydrides.

Willstätter and Waldschmidt-Leitz, who found that the hydrogenating activity of Platinum-black depended upon the presence of occluded Oxygen, employed the reaction with acidified Potassium iodide as a quantitative estimate of the amount of Oxygen present (*Ber.*, 1921, 54 B, 113). When Platinum-black was completely deoxygenated, its catalytic hydrogenating action was entirely absent. Such an inert Platinum-black was, however, immediately reactivated by admitting Oxygen, which it vigorously adsorbed. Platinum-black was deoxygenated by suspending in a solvent, such as Acetic acid, and shaking with Hydrogen at the ordinary temperature for 30 hours, or at 50–60° C. for 8 hours. After this treatment, the metal was quite insoluble in Hydrochloric acid, did not liberate Iodine from Potassium iodide, and even the most easily hydrogenated substances—olefinic or di-olefinic (*e.g.*, Cyclohexene, Limonene)—failed completely to be reduced until the catalyst had again been "primed" with Oxygen. Deoxygenation by evacuation could only be accomplished with difficulty, but in a high vacuum the catalyst gradually became less active for the more difficult hydrogenations. For example, evacuation of Platinum-black for $\frac{1}{2}$ hour at the ordinary

temperature did not markedly alter its activity for the hydrogenation of Benzene. Evacuation for 8 hours very considerably diminished its activity, while 3 hours' evacuation at 100° C. almost completely suppressed it.

The poisonous action towards Platinum of certain easily oxidised organic bodies (*e.g.*, Glycerol, and, to a less degree, Sulphur compounds such as Thiophene) was traced to the ability which these substances possess of deoxygenating the catalyst. The poisoning in these cases was largely overcome by using more catalyst, or by repeatedly loading it with Oxygen. During the hydrogenation of certain substances which reacted with Hydrogen less easily than Benzene, instances of poisoning were observed which were overcome by greatly increasing the amount of catalyst and starting the hydrogenation by adding Benzene. Deoxygenation cannot, however, be regarded as the general mode of action of poisons even in the case of Platinum.

Palladium sponge, when active, also contains Oxygen, and deoxygenation renders it inert, even for reduction of di-olefinic substances. The same is also true for colloidal solutions of Platinum and Palladium. Oxygen is necessary for their hydrogenating activity, which explains the large quantities of catalyst which Skita found necessary for difficult hydrogenations, and Paal's early observation, that an old and partially oxidised specimen of Palladinosol was much more active than other fresher preparations.

Nickel, also, apparently requires for its activity the presence of Oxygen, or an oxide of Nickel, agreeing with the results obtained by Ipatiev, and later ones by Bedford and Erdmann, Brochet and others (*q.v.*). Thus the lower oxides of Nickel produced from Nickel oxide and Hydrogen below 300° C. are powerful hydrogenators, while elementary Nickel prepared at 350° C. is not. This inert metal is, however, activated and made capable of inducing reduction of Sodium cinnamate, Oleic acid, or Methyl oleate, if Oxygen is supplied, of which exceedingly little suffices. Many investigators have sought to explain this action of Oxygen by postulating the formation of sub-oxides, which are assumed to be the active agents. Though definite evidence of the existence of such oxides has in some cases been obtained, proof that they are the essential catalysts is entirely lacking, the available evidence merely justifying the non-committal conclusion that Oxygen is a "promoter" whose presence is necessary for catalytic hydrogenation.

The importance of these observations of Willstätter is very considerable. Priming a Platinum catalyst with Oxygen counteracts the anti-catalytic action of many impurities, and also makes it possible to hydrogenate certain substances (*e.g.*, Phthalic anhydride) which cannot be hydrogenated by any other method. Much less

catalyst, too, can be employed than was originally considered necessary, 0.1–0.2 gram of Platinum generally sufficing per 5–10 grams of substance undergoing reduction. As fatigue sets in this can be cured by recharging with Oxygen, fatigue being the symptom of deoxygenation.

Willstätter and Waldschmidt-Leitz believed the loss of Oxygen—or the onset of fatigue which always occurred during hydrogenation—to proceed at a uniform speed, and compared the reactivities of various reducible substances by measuring the volume of Hydrogen absorbed in the time during which the same weight of catalyst became exhausted. Thus, the following volumes of Hydrogen were transferred by 0.1 gram of Platinum-black, acting at 20° C. :—

- 9 Litres to Cyclohexane,
- 1.2 Litres to Benzene,
- 0.04 Litre to Pyrrole,
- 0.03 Litre to Phthalic anhydride.

Measuring the initial reaction velocities of hydrogenation gave a similar series.

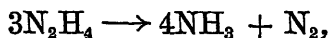
Hydrogenations can therefore be roughly classified on this basis. Using 0.1–0.2 gram of Platinum per 5–10 grams of substance, activation is very rarely necessary during hydrogenation of olefinic substances, since this reaction occurs so much more rapidly than deoxygenation. Other substances are fairly quickly hydrogenated, but not so rapidly that activation can be dispensed with unless large quantities of catalyst are used. Thus, during the hydrogenation of simple aromatic substances, hourly activation is usually preferable. In the third class are those cases where hydrogenation cannot be effected except by frequent reactivation of the catalyst, since deoxygenation occurs at a rate commensurable with hydrogenation. In this way, Willstätter and Waldschmidt-Leitz hydrogenated various substances—chiefly polynuclear aromatic compounds and bodies which directly remove Oxygen from the catalyst—which resisted hydrogenation by any other known method. The reaction was generally carried out at about 60° C., but considerable Hydrogen pressure was not necessary. Activation was effected by disconnecting the shaking apparatus from the Hydrogen supply, evacuating, and admitting air. On shaking, Oxygen was rapidly taken up. When absorption of Oxygen ceased the apparatus was again evacuated, and, after a few minutes, reconnected to the Hydrogen supply, and hydrogenation recommenced. During active Hydrogen transference, and especially immediately after charging with Oxygen, the Platinum was finely divided and powdery. When absorption of Hydrogen slowed down or ceased, the Platinum tended to gather in thick

flocks, which became especially marked when, during a hydrogenation, the adsorbed Oxygen was completely consumed.

The influence of the solvent on rate of hydrogenation was shown by Willstätter and Waldschmidt-Leitz not to be due to differences of solubility of Hydrogen and Oxygen, since Acetic acid, the most energetic medium for hydrogenating, is by no means the best solvent for these gases.

Palladium has no advantages over Platinum and several disadvantages, due to its great adsorptive power for Hydrogen, which make it difficult to activate and maintain active with Oxygen.

Differences in the catalytic behaviour of Platinum and Palladium, according to the presence or absence of Oxygen, had been previously noted by Purgotti and Zanichelli (*Gazz.*, 1904, 34, i, 57) and Hess (*Ber.*, 1913, 46, 3113, 4104). The former investigators confirmed Tanatar's observation that a solution of Hydrazine sulphate decomposes in contact with Platinum-black,



but showed that if the Platinum-black were first boiled with water for 4 hours its power of effecting this reaction was quite lost, though it still caused Hydrogen peroxide and Hydroxylamine to decompose. Heating in a current of Hydrogen, or preparing from a Platinum solution by precipitation with Hydrazine hydrate or Hydroxylamine, likewise gave a "black" which was inert until it had been exposed to air.

Hess, on the other hand, could not hydrogenate certain substituted Pyrroles and obtain satisfactory yields of the Pyrrolidine derivatives except by excluding Oxygen. To hydrogenate Pyrrol 2-β-propanol, $\text{CH} \begin{array}{c} \text{CH} \cdot \text{CH} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{C} \cdot \text{CHOH} \cdot \text{CH}_3$, to Pyrrolidyl 2-isopropyl

alcohol, a glacial Acetic acid suspension of Platinum-black was first saturated with Hydrogen, and the Acetic acid solution of the Pyrrol 2-propanol, similarly treated, then added. On passing Hydrogen at a slightly increased pressure and vigorously agitating, the hydrogenation slowly occurred during $4\frac{1}{2}$ days without the formation of any Pyrrole dyestuffs which, in presence of Oxygen, were formed by catalytic oxidation. Hess' observation is not really at variance with the results obtained by Willstätter, since the treatment described by Hess would not suffice completely to deoxygenate the Platinum-black.

Easy Hydrogenations

This class comprises those hydrogenation reactions that proceed at a rate so much faster than deoxygenation of the catalyst that

even when small quantities only of catalyst are used, complete reduction can be obtained without reactivation.

Reduction of Nitro-compounds. Nitrobenzene in alcoholic solution containing Palladium-black is reduced by a current of Hydrogen to Aniline (Paal and Amberger, *Ber.*, 1905, 38, 1409; Gerum, *Diss.*, Erlangen, 1908).

Reduction of Unsaturated Compounds. Substances containing ethylenic or acetylenic linkages, when brought to the liquid form by melting or solution in a suitable solvent, in presence of Platinum or Palladium-black, are easily reduced by a current of Hydrogen at the ordinary temperature and pressure.

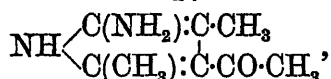
The first reductions of this type were carried out by Fokin, who hydrogenated Oleic, Maleic, Citraconic, and Cinnamic acids to the corresponding saturated acids; Amylene to Pentane and Allyl alcohol to Propyl alcohol (*J. Russ. Phys. Chem. Soc.*, 1907, 39, 607; 1908, 40, 276). Willstätter and Mayer then effected the following hydrogenations: Oleinyl alcohol to Octadecyl alcohol, Ethyl oleate to Stearate, Erucyl alcohol to Docosyl alcohol, and Geraniol, much more slowly, to a mixture of 40 per cent. of 2:6-Dimethyl 8-octanol (Tetrahydro-geraniol) and 60 per cent. of 2:6-Dimethyl octane, $C_{10}H_{22}$. Phytene, $C_{20}H_{40}$, was reduced to Phytane, $C_{20}H_{42}$, Phytol, $C_{20}H_{39}OH$, to a mixture of Dihydrophytol, $C_{20}H_{41}OH$, and Phytane, and Cholesterol, $C_{27}H_{45}OH$, to Dihydrocholesterol, $C_{27}H_{47}OH$, identical with the β -Cholestanol obtained by Diels and Abderhalden from Cholestenone. Ether solutions generally reduced more easily than when no solvent was used (*Ber.*, 1908, 41, 1475, 2199).

Reduction by Willstätter's method is capable of the same sensitive regulation that is possible in Paal's method. Thus, Vavon reduced Carvone in three stages, obtaining successively good yields of the dihydro-body Carvotanacetone, Tetrahydro-carvone, and finally, Carvomenthol (*C.R.*, 1911, 153, 68).

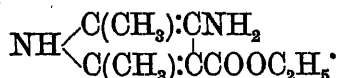
Unsaturated rings and partially reduced aromatic nuclei are easily hydrogenated. Thus Cyclohexadiene in presence of Platinum-black readily absorbs 2 molecules of Hydrogen, giving Cyclohexane (Willstätter and Hatt, *Ber.*, 1912, 45, 1464).

In his researches in the Cyclo-octane series, Willstätter largely employed the catalytic method of reduction. Cyclo-octenone was reduced to Cyclo-octanone, and Cyclo-octatriene to Cyclo-octane. In attempting the preparation of Cyclo-octatetraene, a hydrocarbon, C_8H_8 , was made by heating Dibromo-cyclo-octadiene with Quinoline. Reduction of this substance with Hydrogen in presence of Platinum-black gave a mixture of a Di-cyclo-octane, C_8H_{14} , and Tri-cyclo-octane, C_8H_{12} , proving that bridged rings had been formed during the action at a high temperature between Quinoline and the dibromo-body.

rapid as far as the hydrazo stage, after which the further reduction to amines is slower. In neutral alcoholic solution the reduction practically ceases at the hydrazo stage. In this way, the above azo-dyestuff (III) gave the Amido pyrrole derivative (IV)



and the appropriate azo bodies also gave 4-amino-2 : 3 : 5-Trimethyl pyrrole, $\text{NH} \begin{array}{l} \diagup \text{C}(\text{CH}_3):\text{C}\cdot\text{CH}_3 \\ \diagdown \text{C}(\text{CH}_3):\text{C}\cdot\text{NH}_2 \end{array}$, and 4-amino-2 : 5-dimethyl pyrrole 3-carboxylic ethyl ester,



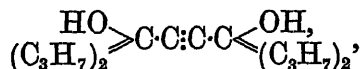
Lespieau reduced the following glycols of the Acetylenic series, $\text{CH}_2\text{OH}\cdot\text{C}:\text{C}\cdot\text{CH}_2\text{OH}$ and $\text{CH}_2\text{OH}\cdot\text{C}:\text{C}:\text{C}:\text{C}\cdot\text{CH}_2\text{OH}$, by dissolving in Alcohol or Ether, and passing Hydrogen in presence of Platinum-black, and obtained good yields of the corresponding saturated glycols. In the latter case, small quantities of Hexane and Hexanol were also obtained by elimination of one or both of the hydroxy groups. Using the dimethyl ethers of these glycols this formation of hydrocarbons was more considerable (*C.R.*, 1910, 150, 1761).

Glycols of the type $\text{HO}\cdot\text{CRR}'\cdot\text{C}:\text{C}\cdot\text{RR}'\cdot\text{OH}$, according to Dupont, are reduced by Palladium-black and Hydrogen to a mixture of the corresponding saturated hydrocarbons, saturated monohydric alcohols, and small amounts of the saturated glycols. Thus,

$(\text{CH}_3)_2 \begin{array}{l} \diagup \\ \diagdown \end{array} \text{C}:\text{C}:\text{C}\cdot\text{C} \begin{array}{l} \diagup \\ \diagdown \end{array} (\text{CH}_3)_2$ gives mainly 2 : 5-Dimethyl hexane, and

2 : 5-Dimethyl hexanol. $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}_2\text{H}_5 \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{C}:\text{C}:\text{C}\cdot\text{C} \begin{array}{l} \diagup \\ \diagdown \end{array} \begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}_2\text{H}_5 \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{OH}$ gives 3 : 6-Dimethyl

octane, with a little of the saturated alcohol. The compound



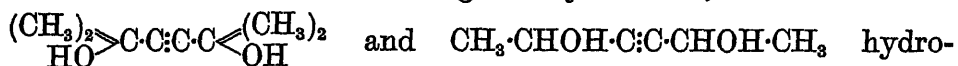
however, gives almost exclusively the Tetrapropyl butane diol.

Aromatic acetylenic glycols are reduced almost quantitatively to the saturated hydrocarbons in presence of Palladium: though in presence of Platinum only the saturated glycols are formed, thus, $\text{C}_6\text{H}_5\text{CHOH}\cdot\text{C}:\text{C}\cdot\text{CHOH}\cdot\text{C}_6\text{H}_5$ gives with Palladium, Diphenyl butane,

while $\begin{array}{c} \text{HO} \\ \diagup \\ \text{CH}_3 \\ \diagdown \\ \text{C}_6\text{H}_5 \end{array} \begin{array}{l} \diagup \\ \diagdown \end{array} \text{C}:\text{C}:\text{C}\cdot\text{C} \begin{array}{l} \diagup \\ \diagdown \end{array} \begin{array}{c} \text{OH} \\ \diagup \\ \text{CH}_3 \\ \diagdown \\ \text{C}_6\text{H}_5 \end{array}$ gives 2 : 5-Diphenyl hexane (*C.R.*, 1913,

156, 1623).

The reduction of acetylenic glycols in presence of Platinum and Palladium has also been investigated by Zalkind, who found that



genated rapidly with Palladium as catalyst until 2 atoms of Hydrogen were absorbed, corresponding with the formation of the ethylenic glycol, after which further hydrogenation was slow. Platinum, however, induced rapid hydrogenation at a steady pace, giving the saturated glycol, after which prolonged action tended to replace the

hydroxy-group. $\begin{array}{c} (\text{CH}_3)_2 \\ \text{HO} \end{array} \text{C} \text{C} \text{C} \text{C} \text{C}_6\text{H}_5$ could not be partially hydrogenated, and gave only the saturated body (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1875; 1914, 46, 1527; 1915, 47, 680, 2045).

Madinaveitia has investigated the catalytic activity of the other finely-divided metals of the Platinum group (*Ann. Soc. Espan. fis. quim.*, 1914, 11, 328). Ruthenium and Rhodium-black were made by reduction of the chlorides, and tested for hydrogenation of Cinnamic acid and Toluene in glacial Acetic acid solutions. The former slowly hydrogenated Cinnamic acid, but had no action on Toluene: the latter effected hydrogenation of both. Osmium-black, prepared by reduction of Osmic acid in the cold with Formic acid, did not even hydrogenate Cinnamic acid. Iridium-black, prepared by reduction of the chloride with Formic acid, slowly reduced Cinnamic acid, but induced no hydrogenation of Toluene.

The following unsaturated substances also have been reduced by Platinum or Palladium-black:—

Safrole, isoSafrole, Eugenol, isoEugenol, Crotonaldehyde (Fournier, *Bull. Soc. chim.*, 1910, (4), 7, 23). The diacetylenic dicarboxylic acid, $\text{COOH} \cdot \text{C} \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \text{C} \cdot \text{COOH}$ (Lespieau and Vavon, *C.R.*, 1909, 148, 1335). Dimethyl granatanine, Tropicine, Base $\text{C}_8\text{H}_8 \cdot \text{NH}(\text{CH}_3)_2$; 2-Cyclo-4²-cyclo-octenone (Granatal), Cyclo-octatriene, Cyclo-octatetraene (Willstätter and Waser, *Ber.*, 1910, 43, 1176; 1911, 44, 3423). Pinene; Camphene; Limonene; French, German, and American Turpentine (mostly α - and β -Pinenes); Maleic, Fumaric, Cinnamic, and Erucic acids (Vavon, *C.R.*, 1909, 149, 997; 1910, 150, 1127; 1911, 152, 1675; *Bull. Soc. chim.*, 1911, 9, 256). Isomeric α - and β -Cholesterylenes (Tschugaev and Fomin, *C.R.*, 1910, 150, 1435). Vinyl trimethylene (Philipov, *J. Russ. Phys. Chem. Soc.*, 1912, 44, 469). Santonin (Wienhaus and V. Oettingen, *Ann.*, 1913, 397, 219; Wedekind and Beniers, *ibid.*, 1913, 397, 246; Bargellini, *Atti R. Accad. Lincei*, 22, I, 443; Cusmano, *ibid.*, 22, I, 711. See also *Ber.*, 1913, 46, 1775); Urushiol, $\text{C}_{20}\text{H}_{32}\text{O}_2$, from Japanese lac, Dimethyl urushiol, Eleostearic acid (Majima, *Ber.*, 1912, 45, 2727).

Aldehydes and Ketones

Chemical methods of reduction, using such agents as Sodium amalgam and water, usually give inferior yields of alcohols from aldehydes or ketones. On the other hand, the carbonyl group is easily reduced to the primary or secondary alcoholic group by passing Hydrogen at the ordinary, or slightly raised temperature and pressure through a solution of the aldehyde or ketone in a suitable solvent (Ether, Alcohol, water, or Acetic acid) containing Platinum or Palladium-black in suspension. The generalisation of the method to aldehydes and ketones is due to Vavon, who showed that all classes, aliphatic, cyclic, aromatic, ethylenic, and terpenic, were reduced almost quantitatively if the conditions were suitably regulated. The best solvent depends upon the particular aldehyde or ketone undergoing reduction. Pinacones are never formed, but if reduction conditions are too drastic, or the reaction is too prolonged, it proceeds beyond the alcohol stage, with formation of a hydrocarbon. Aromatic carbonyl compounds are especially prone to this further change, giving, as in the Sabatier and Senderens method, the aromatic or hydroaromatic hydrocarbon containing an equal number of Carbon atoms.

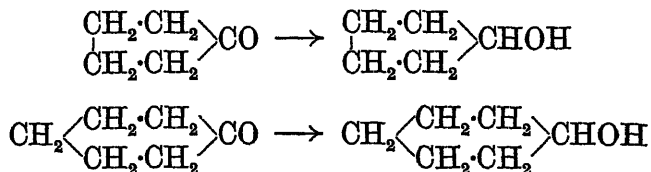
Acetaldehyde, $\text{CH}_3\cdot\text{CHO}$, in water gives Ethyl alcohol, $\text{C}_2\text{H}_5\cdot\text{OH}$. isoValeric aldehyde, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CHO}$, in Ether or Acetic acid gives isoAmyl alcohol, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, and Heptaldehyde in ether is reduced to Heptyl alcohol, $\text{C}_7\text{H}_{15}\cdot\text{OH}$. Citral in ether similarly is reduced to a mixture of the alcohol 2:6:8-Dimethyl octanol, the hydrocarbon, 2:6-Dimethyl octane, and a third substance, not identified (Vavon, *Ann. Chim.*, 1914, IX, 1, 144). Crotonic aldehyde, $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CHO}$, similarly gives Butyric aldehyde, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO}$, and Butyl alcohol (Fournier, *Bull. Soc. chim.*, 1910, (4), 7, 23).

Aqueous acetone easily reduces to isoPropyl alcohol, Methyl ethyl ketone, $\text{CH}_3\cdot\text{CO}\cdot\text{C}_2\text{H}_5$, in water or Acetic acid, to Methyl ethyl carbinol, and Diethyl ketone, $(\text{C}_2\text{H}_5)_2\text{CO}$, or Methyl propyl ketone, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$, in Acetic acid to Diethyl carbinol, $(\text{C}_2\text{H}_5)_2\text{CH}\cdot\text{OH}$, or Methyl propyl carbinol, $\text{CH}_3\cdot\text{CHOH}\cdot\text{C}_3\text{H}_7$, respectively. Mesityl oxide, $(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CO}\cdot\text{CH}_3$, reduces in two stages, giving first Methyl isobutyl ketone, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$, and then Methyl isobutyl carbinol, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CHOH}\cdot\text{CH}_3$, according to the conditions of the reaction.

Acetyl acetone, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$, in water, ether, or alcohol, gives a mixture of an Amyl alcohol, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHOH}\cdot\text{CH}_3$, and the Glycol, $\text{CH}_3\cdot\text{CHOH}\cdot\text{CH}_2\cdot\text{CHOH}\cdot\text{CH}_3$, while Ethyl acetoacetate, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5$, alone, or in ether, behaves similarly, and gives a mixture of the hydroxy ester, $\text{CH}_3\cdot\text{CHOH}\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5$,

with a little Butyric ester, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOC}_2\text{H}_5$ (Vavon, *C.R.*, 1912, 155, 286; *Ann. Chim.*, 1914, IX, 1, 144).

Cyclic ketones are equally smoothly reduced to the secondary alcohols. Thus, Cyclopentanone and Cyclohexanone in ether solution are reduced to Cyclopentanol and Cyclohexanol,



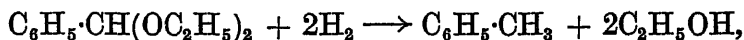
Pulegone and 1-Menthone give the same Menthol; and Carvone, as we have seen, reduces in three stages, giving finally Carvomenthol (Vavon, *C.R.*, 1912, 155, 286).

✓ Aromatic aldehydes in general give quantitatively the corresponding aromatic alcohols when dissolved in about 3 parts of Ether, Ethyl acetate, or Methyl or Ethyl alcohols containing a few grams of Platinum-black, and shaken with Hydrogen at the ordinary pressure. Vavon reduced the following: Benzaldehyde, $\text{C}_6\text{H}_5\cdot\text{CHO}$; Salicylaldehyde, $\text{C}_6\text{H}_4\cdot\text{OH}\cdot\text{CHO}$ (ortho); Salicylaldehyde methyl ether, $\text{C}_6\text{H}_4\cdot\text{OCH}_3\cdot\text{CHO}$ (ortho); Benzoyl salicylaldehyde, $\text{C}_6\text{H}_4\cdot\text{OCOC}_6\text{H}_5\cdot\text{CHO}$ (ortho); para-Anisicaldehyde, $\text{C}_6\text{H}_4\cdot\text{OCH}_3\cdot\text{CHO}$; Vanillin, the Methyl, Ethyl, Acetyl, and Benzoyl derivatives of Vanillin, Piperonal, and Cinnamic aldehyde (*C.R.*, 1912, 154, 359). The almost quantitative reduction to alcohol obtained by the Willstätter method is in strong contrast with the results at higher temperatures, as in the Sabatier and Senderens and Ipatiev methods, where only more completely reduced products, aromatic and hydro-aromatic hydrocarbons, can be isolated. The same complete reduction to hydrocarbon may, however, be obtained in Willstätter's method when Acetic acid is used as solvent. ✓

Aromatic ketones similarly are reduced to secondary alcohols. ✓ Acetophenone, $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_3$, in 60 per cent. aqueous alcohol gives almost pure Phenyl methyl carbinol, $\text{C}_6\text{H}_5\cdot\text{CHOH}\cdot\text{CH}_3$; but in ether, pure Alcohol, Ethyl acetate, or Acetic acid, reduces more completely, finally absorbing 10 atomic proportions of Hydrogen, and giving Cyclohexyl ethane, $\text{C}_6\text{H}_{11}\cdot\text{CH}_2\cdot\text{CH}_3$. Benzophenone, $(\text{C}_6\text{H}_5)_2\text{CO}$, in Ether gives in the same way Benzhydrol, $(\text{C}_6\text{H}_5)_2\cdot\text{CHOH}$ (Vavon, *C.R.*, 1912, 155, 286).

Suzuki Kariyone and Kimura passed Hydrogen into glacial Acetic acid solutions of various acetals and ethers, containing as catalyst Palladium mounted on Barium sulphate (*J. Pharm. Soc. Japan*, 1923, 746). In each case, when an aldehydic group, $\cdot\text{CHO}$, or its derived acetal was united directly to an aromatic ring, reduction to

the group $\cdot\text{CH}_3$ occurred. Thus, Benzaldehyde acetal gave Toluene almost quantitatively,



and the diethyl acetals from para-Methoxybenzaldehyde and para-Tolylaldehyde behaved in the same way. On the other hand, when the etherified aldehyde group was not directly attached to a benzene ring, then this reduction did not take place, as in the cases of acetals from Cinnamic and isoValeric aldehydes, Acetophenone, and Benzoic acid triethyl ether.

Three intermediate stages of reduction of Benzylidene acetone, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CH}_3$, were isolated by Vavon (*C.R.*, 1912, 154, 1705). By dissolving 13 grams in 30 grams of ether, adding Platinum-black, agitating in a stream of Hydrogen, and stopping when the requisite volume of Hydrogen had been absorbed, the following products were obtained. (1) Phenyl butanone, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$, by saturation of the double linkage. (2) Phenyl butanol, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHOH}\cdot\text{CH}_3$, by reduction of the keto-group, (3) Cyclohexyl butanol,



by hydrogenation of the aromatic nucleus. The relative ease with which these three types of reaction proceed can be gauged from the times required: the first stage required 6 minutes, the first two stages 17 minutes, and the three stages were completed in 130 minutes. Benzylidene camphor was similarly reduced.

Sugars can also be reduced. A 25 per cent. solution of *d*-Glucose (200 c.c.) in 0.5*N*-Caustic potash solution with about 3 grams of Platinum-black was reduced by Cake in about 18 hours to a mixture of *d*-Sorbite and *d*-Mannite. In neutral solution, reduction was stated not to take place (*J. Am. C.S.*, 1922, 44, 859).

More Difficult Hydrogenations

Here are included those hydrogenations which can be carried out by the use of a considerable proportion of catalyst without activation, or by a small quantity, activating at intervals. Most simple aromatic and heterocyclic substances can be hydrogenated in this way. Partially hydrogenated derivatives are not produced.

Benzene, Toluene, and Ethyl benzene give Cyclohexane, Methyl, and Ethyl cyclohexanes, respectively (Vavon, *C.R.*, 1912, 154, 1705). Willstätter and Hatt showed, however, that the Benzene must be free from Thiophene, or no absorption of Hydrogen can be obtained. Using pure Benzene, at the ordinary temperature, without a solvent, and Hydrogen at slightly reduced pressure, 0.6 part of Platinum produced quantitative reduction in 7 hours. The favourable influence

of a promoting solvent was illustrated by the fact that when the Benzene was diluted with Acetic acid, reduction was complete in 6 hours, using only 0.1 part of Platinum. Less than 0.001 per cent. of Thiophene prevented reduction (*Ber.*, 1912, 45, 1471).

Toluene, Xylene, and Durene (1 : 2 : 4 : 5-Tetramethyl benzene) were similarly reduced, action, however, becoming slower as the number of substituent groups increased. Phenyl ethylene, $C_6H_5 \cdot CH : CH_2$, can easily be reduced in stages, giving successively Ethyl benzene and Ethyl cyclohexane (Willstätter and King, *Ber.*, 1913, 46, 527).

Benzoic acid, until purified, can only be partially reduced, but the pure substance in ether solution can be hydrogenated quantitatively to Cyclohexane carboxylic acid, $C_6H_{11} \cdot COOH$.

Phenol, in Acetic acid, gives a mixture of 60 per cent. of Cyclohexanol and 40 per cent. of Cyclohexane; Aniline in 80 hours is reduced, giving mostly Dicyclohexylamine, $(C_6H_{11})_2NH$, with some 10 per cent. of Cyclohexylamine, $C_6H_{11} \cdot NH_2$. The purest commercial Naphthalene resisted hydrogenation, and was then found to contain 0.25 per cent. of Sulphur. After purification by repeated crystallisation it reduced easily, and without a solvent, directly to Decahydronaphthalene. In Acetic acid solution, the same product was obtained in a much shorter time. By interrupting the passage of Hydrogen after the absorption of four atomic proportions, the product was a mixture of unchanged Naphthalene and the decahydro-derivative, and Tetrahydronaphthalene could not be isolated. By hydrogenation of Dihydronaphthalene, however, a marked decrease in the rate of absorption occurred when two atomic proportions had been taken up, and an almost pure tetrahydro-body was isolated (Willstätter and King, *Ber.*, 1913, 46, 527). In a later investigation partial hydrogenation of Naphthalene to Tetrahydronaphthalene was easily achieved. These unexpected differences were explained when the influence of Oxygen in the process of hydrogenation came to be recognised: the rapid hydrogenation by the use of Platinum sponge rich in Oxygen easily enabling the intermediate tetrahydro-stage to be isolated (Willstätter and Seitz, *Ber.*, 1923, 56 B, 1388).

Halogen compounds can be partially reduced before the activity of the catalyst is destroyed. Thus, with Chlorotoluene, reaction proceeds to the absorption of three atomic proportions of Hydrogen, with simultaneous evolution of Hydrochloric acid. Allyl bromide behaves similarly.

Pure Pyrrole in Acetic acid solution, but not in Ether, was slowly hydrogenated to Pyrrolidine. Presence of Sulphur inhibited the reaction. isoHæmopyrrole was similarly hydrogenated. Pyrrole and certain of its derivatives were also hydrogenated by Hess, who found that the presence of appreciable quantities of Oxygen was pre-

judicial to a good yield. Pyrrol 2-propanol, $\begin{array}{c} \text{CH}-\text{CH} \\ | \quad | \\ \text{CH} \quad \text{C}-\text{CH}_2 \cdot \text{CHOH} \cdot \text{CH}_3, \\ | \\ \text{NH} \end{array}$

in glacial Acetic acid solution, with Hydrogen, in contact with Platinum or Palladium sponge, gave in $4\frac{1}{2}$ days the corresponding Pyrrolidyl 2-propanol, whilst Pyrrol 2-propane- $\beta\gamma$ -diol,

$\begin{array}{c} \text{CH}-\text{CH} \\ | \quad | \\ \text{CH} \quad \text{C}-\text{CH}_2 \cdot \text{CHOH} \cdot \text{CH}_2\text{OH}, \\ | \\ \text{NH} \end{array}$ reduced in the same way to Pyrrolidyl

2-propane- $\beta\gamma$ -diol (*Ber.*, 1913, 46, 3113, 4104). Under certain conditions, especially using Palladium, reduction extended to the side-chain, with formation of a certain amount of 2-Propyl pyrrolidine.

Phenanthrene in ether solution was hydrogenated by Schmidt and Fischer to the dihydride at the ordinary temperature in 2 days, and at the boiling point of ether in 8 hours (*Ber.*, 1908, 41, 4225). Breteau, using Phenanthrene in Cyclohexane solution, obtained the tetrahydride using a Palladium catalyst, but with a Platinum catalyst could obtain no action.

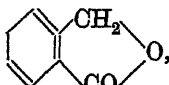
Fluorine Derivatives

The reduction of aromatic Fluorine derivatives in presence of Hydrogen and Platinum-black has been studied by Swartz (*Bull. Acad. roy. Belg.*, 1920, 399), who showed that the reaction is different according to whether the Fluorine is in the aromatic nucleus or in a side-chain. If the Fluorine is attached to the nucleus, the first effect of reduction is to displace it. Thus, para-Fluorobenzoic acid, $\text{F} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH}$, hydrogenated in aqueous solution, as its sodium salt, gives two distinct stages, first Benzoic acid, $\text{C}_6\text{H}_5 \cdot \text{COOH}$, and then Hexahydrobenzoic acid, $\text{C}_6\text{H}_{11} \cdot \text{COOH}$, more slowly. Fluorobenzene similarly reduces in two stages, though they are not so well defined. Cyclohexane is the final product. Silicon tetrafluoride or Hydrofluoric acid does not affect the catalyst's activity. When the Fluorine is in a side-chain, Cyclohexane derivatives may be obtained without eliminating the Fluorine. For example, Trifluorotoluene, $\text{C}_6\text{H}_5 \cdot \text{CF}_3$, gives exclusively Trifluoromethyl cyclohexane, $\text{C}_6\text{H}_{11} \cdot \text{CF}_3$. Difluorotoluene, $\text{C}_6\text{H}_5 \cdot \text{CHF}_2$, gives mainly Difluoromethyl cyclohexane, with a little Methyl cyclohexane, from which it would appear that the $\cdot\text{CHF}_2$ group is rather less stable than the $\cdot\text{CF}_3$ group. Difluorochlorotoluene reduced in the same way gives Difluorotoluene, $\text{C}_6\text{H}_5 \cdot \text{CHF}_2$, Toluene and Methyl cyclohexane, so that the additional presence of Chlorine in the side-chain has rendered the Fluorine more labile.

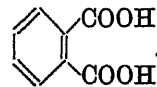
Difficult Hydrogenations

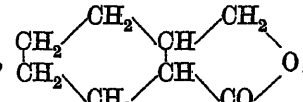
Willstätter and Jaquet found that by repeated priming with Oxygen of Platinum-black, suspended in Acetic acid, certain hydrogenations could be effected which are not possible by any other method (*Ber.*, 1918, 51, 767).

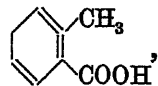
Phthalic anhydride (20.3 grams) was dissolved in glacial Acetic acid (74 c.c.), Platinum-black (5 grams) added, and the solution shaken with Hydrogen. Only 400 c.c. were absorbed. When the Hydrogen in the reaction vessel was replaced by air and the shaking continued, 25 c.c. of Oxygen were rapidly absorbed. On recommencing hydrogenation, a further 500 c.c. of Hydrogen were taken up before the catalyst again became inert. After alternately oxygenating and hydrogenating some 20 times, the total absorption of Hydrogen amounted to 17,040 c.c. (measured at laboratory temperature and pressure), or, deducting 1150 c.c. necessary for combination with the Oxygen introduced, about 4.8 molecular proportions. The hydrogenation took the following course. The anhydride ring was

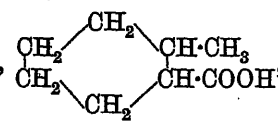
first attacked, giving Phthalide, , whilst the water

formed at the same time hydrolysed some of the Phthalic anhydride

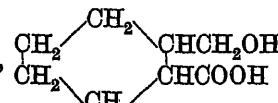
to Phthalic acid, . The Phthalide then reduced in two

ways, part producing Hexahydrophthalide, , the remainder splitting in the anhydride ring, producing ortho-Toluic acid,

, which further hydrogenated to Hexahydro-ortho-

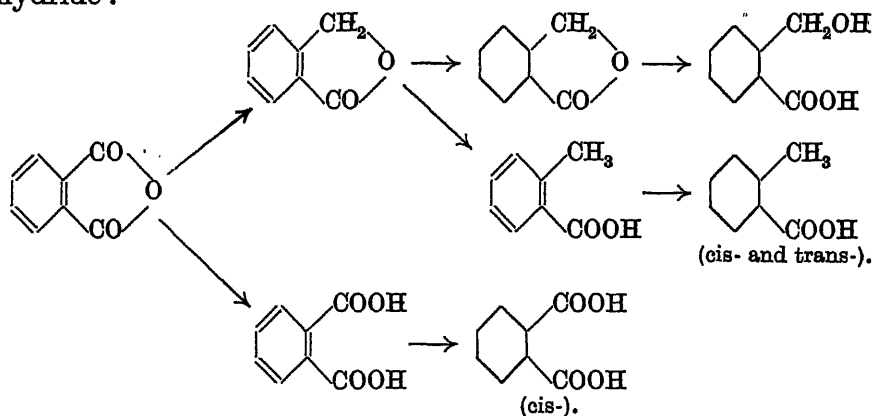
toluic acid, , forming both cis- and trans-isomers.

The Phthalic acid produced in the first stage of the process also hydrogenated, giving cis-Hexahydrophthalic acid; and since alkalis were used in the separation of the products of reduction, a part of the Hexahydrophthalide was converted by hydrolysis into

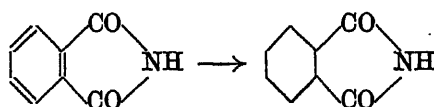
Methylol hexahydrobenzoic acid, . It was noticed

that, whilst Phthalide can be reduced by activated Platinum to ortho-

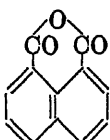
Toluic acid, Hexahydrophthalide is stable, and does not undergo the analogous change to Hexahydro-ortho-toluic acid. Thus, Phthalide was submitted to hydrogenation with repeatedly activated Platinum. 3-4 Molecular equivalents of Hydrogen were taken up, and a mixture of approximately equal parts of Hexahydrophthalide and Hexahydro-ortho-toluic acid was formed. The following scheme represents the complete reduction of Phthalic anhydride :—



Phthalimide when subjected to hydrogenation in Acetic acid solution gave Hexahydrophthalimide, only the aromatic nucleus being attacked,

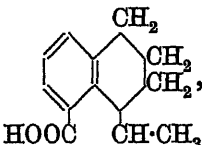


Other solvents, such as Methyl or Ethyl alcohol, or Cyclohexane, could not be used. With the most active preparation of Platinum sponge, this hydrogenation could be very slowly carried out without activation, but much more slowly than the hydrogenation of Benzene, and many preparations of catalyst were found sufficing for Benzene that were inert with Phthalimide.

Naphthalic anhydride, , like Phthalic anhydride, could

only be hydrogenated when activated Platinum was employed, and the course of the reaction was similar. The anhydride ring was first attacked, and the action perceptibly slowed after the absorption of four atomic proportions of Hydrogen. The products were Tetrahydro- and Decahydro-naphthalides, Tetrahydronaphthalic acid, formed by hydrolysis of a part of the Naphthalic anhydride and

subsequent hydrogenation, Tetrahydro-1-methylnaphthalene 8-carb-

oxylic acid, , and Decahydro-acenaphthene.

Willstätter and Jaquet also observed several remarkable cases of catalytic inhibition, traced to the presence of acid anhydrides. Thus, many carboxylic acids—and even Benzene itself—which are easily hydrogenated when pure, could not be hydrogenated with the same specimen of catalyst when traces of acid anhydrides were present, unless the Platinum was first strongly activated with Oxygen. For example, Naphthalic acid, purified by recrystallisation from alcohol, could not be hydrogenated except by repeated activation of the catalyst, whereas when freshly precipitated from solutions of Naphthalates reduction proceeded normally. Unlike Naphthalene itself, Naphthalic acid adds only 4 atoms of Hydrogen, forming Tetrahydronaphthalic acid.

Phthalic acid in Acetic acid, when quite free from the anhydride, was easily hydrogenated to pure cis-Hexahydrophthalic acid. The pure para-Dicarboxylic (Terephthalic) acid, when suspended with Platinum-black in Acetic acid likewise gave fairly easily, on warming, a mixture of about equal parts of the cis- and trans-Hexahydro acids. The meta-Dicarboxylic (isoPhathlic) acid often contained traces of Phthalic anhydride which inhibited reduction, but the pure acid, suspended in Acetic acid, was easily reduced to a mixture of cis- and trans-Hexahydro-isophthalic acids. The reduction of para-Toluic acid was similar. When pure, a mixture of cis- and trans-Hexahydrotoluic acids was easily produced: whereas in the presence of acid anhydrides the hydrogenation was much more difficult and only possible by frequent oxygenation of the catalyst.

The shortage of higher fatty acids in Germany following the war led Willstätter to consider the possible use of the alkali salts of hydrogenated aromatic acids as substitutes in the manufacture of soap (Willstätter and Waldschmidt-Litz, *Ber.*, 1921, 54 B, 1420). ortho-Benzoylbenzoic acid, $C_6H_5 \cdot CO \cdot C_6H_4 \cdot COOH$, and ortho- α -Naphthoylbenzoic acid, $C_{10}H_7 \cdot CO \cdot C_6H_4 \cdot COOH$, with Hydrogen, and frequently activated Platinum, gave the corresponding Perhydrodiaryl methane carboxylic acids, the $:CO$ group reducing to $:CH_2$ and the aromatic nucleus hydrogenating to saturation. These two stages of the reaction can be easily separated, the intermediate compounds ortho-Benzylbenzoic acid, $C_6H_5 \cdot CH_2 \cdot C_6H_4 \cdot COOH$, and α -Naphthyl methane ortho-Benzoic acid, $C_{10}H_7 \cdot CH_2 \cdot C_6H_4 \cdot COOH$, being easily formed, while further hydrogenation is only effected with the aid of Platinum frequently activated. The Perhydronaphthyl derivative

conferred soapy properties—though much less considerably than Stearic acid. Its use was protected in D.R.-P. 325714. Diphenyl acetic acid, $(C_6H_5)_2CH\cdot COOH$, hydrogenated without the necessity of repeated activation, to Perhydrodiphenyl (Dicyclohexyl) acetic acid, $(C_6H_{11})_2CH\cdot COOH$, but the Sodium salt was useless as a substitute for soap.

Inorganic Reductions

Several catalytic actions of finely-divided metals have been investigated by K. A. Hofmann and collaborators. Thus, Hofmann and Schneider have shown that Sodium chlorate solution in presence of finely-divided catalytic metals slowly absorbs Hydrogen. The activity of the metals for reduction of chlorate with Hydrogen is in the order Pt, Rh, Ru, Pd, Au, Os, Ir, Ag.

The same metals bring about the oxidation of Carbon monoxide to Carbon dioxide by means of Sodium chlorate solution, their activity in this reaction being in the order Os, Rh, Au, Pt, Ru, Pd, Ir, Ag; Methane and Ethylene are hardly affected by the oxidising agent in any case (*Ber.*, 1913, 46, 1657; 1915, 48, 1585; 1920, 53 B, 298).

By suspending spongy Platinum, and passing Hydrogen, Gall and Manchot have effected the following reductions in aqueous solutions. Nitric acid to Nitrous acid and Ammonia; ferricyanides to ferrocyanides; Ferric chloride to Ferrous chloride; Cupric chloride to Cuprous chloride; pentavalent or quadrivalent Vanadium compounds to tervalent; chlorates, iodates, and periodates to chlorides or iodides, and the free halogens to the corresponding halogen acids. Perchlorates were not reduced (*Ber.*, 1905, 58, 482).

Brochet's Researches

The investigations of Ipatiev, Paal, Skita, and Willstätter show that hydrogenation can be effected by "base" metals at high temperatures and Hydrogen pressures, or by "noble" metals at temperatures and pressures at about the atmospheric. Brochet, using base metal or oxide catalysts, compromised between the drastic experimental conditions of Ipatiev and the easy conditions of the other investigators, and showed that Nickel, in particular, is capable of effecting many hydrogenations, especially of unsaturated groupings, at temperatures and pressures of Hydrogen not far removed from the ordinary (*C.R.*, 1914, 158, 1351; *Bull. Soc. chim.*, 1914, IV, 15, 554).

The apparatus employed for laboratory investigations consisted of a lagged Copper autoclave of about 1200 c.c. capacity, arranged for electrical heating and fitted with a cover carrying a stirrer, pressure gauge, and thermometer socket. The substance to be reduced, either alone or dissolved or suspended in a suitable liquid

medium, was then introduced, one-half to two-thirds filling the autoclave, together with a quantity (5 per cent. or more) of active catalyst, usually Nickel. Hydrogen up to a pressure of 15–20 atmospheres was then applied through a valve from a cylinder, or store of compressed Hydrogen, and the autoclave heated, meantime observing the progress of reaction by the movement of the pressure gauge. When much Hydrogen was absorbed, an addition during the reaction was necessary, which was sometimes arranged to be supplied automatically by means of a reducing valve between the Hydrogen cylinder and the autoclave.

In the case of most unsaturated substances, it was found that hydrogenation occurred slowly at the ordinary pressure, and that the rate of reaction could be enormously augmented by vigorous agitation. The liquid or solution undergoing this treatment was enclosed in a glass vessel of about 500 c.c. capacity, the catalyst added, and the vessel closed by a gas-tight cover, carrying inlet and outlet tubes, a thermometer, and stirring mechanism. The reaction was effected by heating the reactants to the desired temperature, passing Hydrogen, and driving the stirrer at a sufficient speed to beat the liquid into a fine spray (1000–1500 r.p.m.).

A modification of this method due to Rather and Reid is claimed to be especially suitable for the hydrogenation of volatile substances. By passing with Hydrogen into a heated non-volatile solvent, such as paraffin, at 180° C., agitated by a stirrer rotating at 3300–3800 r.p.m., and containing in suspension Nickel deposited on infusorial earth, good contact between the gases and catalyst is secured, as well as a very equable temperature. A 70 per cent. yield of Ethane was obtained from Ethylene and Hydrogen (*J. Am. C.S.*, 1915, 37, 2115).

✓ The catalyst, usually Nickel, was prepared by Brochet as follows :
1. Commercial hydrated Nickel oxide, containing much carbonate, was calcined to constant weight, and then reduced in a current of electrolytic Hydrogen at 300° C. for 48 hours. The metal so obtained after cooling in Hydrogen was brightly pyrophoric in air, and was a catalyst of very uniform character, but not necessarily of the greatest possible activity. After cooling in a current of Carbon dioxide, the metal was no longer pyrophoric in air at the ordinary temperature, but its catalytic properties were not in any way reduced, and the best results were obtained with metal allowed to cool in Carbon dioxide. The pyrophoric property of finely-divided Nickel cooled in Hydrogen was shown to be due to occluded Hydrogen, and no relation existed between the pyrophoric and catalytic properties of different specimens of Nickel (*C.R.*, 1922, 175, 816, 1073). 2. Calcination at a carefully regulated temperature, and in an inert atmosphere, of an organic Nickel salt containing sufficient Hydrogen to reduce the Nickel to

free metal. Nickel formate, oxalate, acetate, or lactate was used by Brochet, who found that Hydrogen and Carbon dioxide were evolved during the decomposition in approximately the theoretical proportions. The formate decomposed slowly at 160° C., rapidly at 200–250° C., and violently at 270° C., giving a very active and pyrophoric Nickel. The oxalate required a higher temperature, 320–380° C., and the Nickel so obtained was not pyrophoric at ordinary temperatures in air. Cobalt and Iron were made in similar ways, but Iron so prepared possessed only a feeble activity, leading to the view—supported by other evidence—that the lower hydrogenating activity of metallic Iron is an inherent property, and not due to the higher temperatures necessary to reduce its oxides.

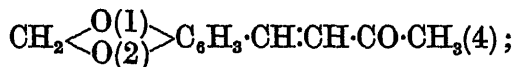
Nickel prepared by either of these methods possesses a high order of activity, and the most recent methods of preparation of active catalytic Nickel on a commercial scale are, in essentials, the same.

Catalysts may with advantage often be made by one of these methods in a liquid medium, or in presence of the substance to be reduced. Thus, if Nickel formate is heated in Cotton-seed oil in an inert or a reducing atmosphere, decomposition of the formate commences at 160° C., and between 160° C. and 250° C. is easily completed, the oil undergoing partial hydrogenation with the Hydrogen liberated. The Nickel is formed in a very active state, and will induce the complete hydrogenation of most oils easily at a temperature of 100° C., with Hydrogen at ordinary pressure (*Bull. Soc. chim.*, 1920, IV, 27, 899).

If a promoter or a support is to be used in conjunction with the catalyst, these are best incorporated by decomposing the Nickel organic salt as before, in intimate admixture with them (E.P. 135510 of 1919), or by precipitating Nickel carbonate with the carbonate of the promoting metal, upon the support, drying, grinding, and reducing. The other hydrogenating catalysts, Cobalt, Iron, and Copper, can be prepared similarly.

Ethylenic and acetylenic linkages are most easily reduced, this often occurring appreciably with Nickel at the ordinary temperature and pressure. Thus, Cotton-seed oil containing a considerable proportion of catalyst, when agitated with Hydrogen, slowly warms and gradually hydrogenates. Nitro-, Nitroso-, Azoxy-, Azo-, and Hydrazo-aromatic compounds are reduced to amines, generally requiring, however, increased Hydrogen pressure and a higher temperature. Aldehydes and ketones, under suitable conditions, give alcohols, while the aromatic nucleus, much more difficult to hydrogenate, requires generally rather more drastic conditions. Presence of a phenolic group, however, facilitates hydrogenation of the aromatic nucleus, so that Phenols and Naphthols under moderate conditions yield hydrogenated derivatives.

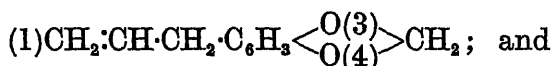
Brochet and Bauer effected the hydrogenation of 1-Octene, $\text{CH}_2:\text{CH}(\text{CH}_2)_6\cdot\text{CH}_3$, to Octane, and Cinnamic acid, Methyl cinnamate, and Sodium cinnamate to the corresponding Phenyl propionic compounds. Likewise the ethylenic linkages in Allyl alcohol, $\text{CH}_2:\text{CH}\cdot\text{CH}_2\cdot\text{OH}$, Piperonylidene ketone,



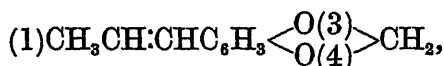
Piperonyl acrylic acid, $\text{CH}_2\begin{smallmatrix} \text{O}(1) \\ \text{O}(2) \end{smallmatrix} \text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COOH}(4)$; Anethole, $\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CH}_3$; Eugenole,



isoEugenole, $(1)\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_3(\text{OCH}_3)(3)(\text{OH})(4)$; Safrole,

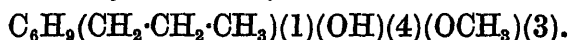


isoSafrole,



were reduced, forming dihydro-derivatives in each case (*C.R.*, 1914, 159, 190; *Bull. Soc. chim.*, 1915, IV, 17, 50). The compounds in the liquid state, or dissolved in a suitable solvent, were mixed with relatively large quantities of catalyst (10–20 grams of Nickel per 100 grams of substance), and agitated with Hydrogen at a pressure of 15 kgm. per sq. cm., at temperatures ranging from 13° C. to 100° C., according to the substance and solvent used. During the reaction, as soon as the pressure fell to 5–8 kgm. per sq. cm., a further charge of Hydrogen was introduced to complete the reduction.

The Octene in Ethyl alcohol solution reduced rapidly at the ordinary temperature. Cinnamic acid (100 grams in 200 grams of Amyl alcohol) at 100° C. was reduced in 1½ hours; or in Ethyl alcohol at 40° C. rather more slowly, in each case dissolving some of the Nickel. This was obviated by the use of the methyl ester dissolved in Methyl alcohol, or of the Sodium salt, dissolved in water, which hydrogenated very easily, giving Sodium phenyl propionate completely in 1 hour at the ordinary temperature. Piperonyl acrylic acid also reduced most easily in the form of its Sodium salt, dissolved in water. Anethole required no solvent, and quickly reduced at 60–80° C., and Eugenole, Safrole, and isoSafrole similarly, while isoEugenole reduced almost as readily at the ordinary temperature. The aromatic bodies would not hydrogenate in the nucleus, on further treatment, even at 200° C., except in the case of Eugenole, which gave eventually the octahydro-derivative,



Cornubert prepared Allyl cyclohexanone, and allyl derivatives of the three Methyl cyclohexanones (*C.R.*, 1914, 158, 1900), and reduced them in the same way to the corresponding propyl derivatives (*C.R.*, 1914, 159, 75).

Brochet and Cabaret then showed that these reductions proceeded with Hydrogen at atmospheric pressure, using large quantities of catalyst, vigorous agitation, and a suitable temperature. Thus, Sodium cinnamate (100 grams) in 200 c.c. of water, at 19–36° C. was completely hydrogenated in 2½ hours. The ethyl ester, in Alcohol, however, required 7 hours at 70° C. Allyl alcohol and *l*-Octene very slowly reduced in presence of large amounts of Nickel. Anethole and isoSafrole, however, at 65–70° C. hydrogenated very rapidly. Ketones could not be converted into secondary alcohols with Hydrogen at the ordinary pressure, but ethylenic linkages in unsaturated ketones were easily reduced (*C.R.*, 1914, 159, 326; *Bull. Soc. chim.*, 1915, IV, 17, 55).

The extension to aldehydes and ketones, using Hydrogen pressures of 10–15 kgm. per sq. cm., and temperatures of 120–130° C., was described by Brochet in F.P. 458033 of 1912, and E.P. 16936 of 1913. Benzaldehyde under these conditions gave Benzyl alcohol, and Acetophenone was reduced to Phenyl methyl carbinol.

A low pressure of Hydrogen, catalytic Nickel and a suitable temperature also reduced aromatic nitro-compounds to amines. Nitrobenzene at 100° C. in an autoclave, vigorously stirred with Nickel, and Hydrogen at 10–15 kgm. per sq. cm., was quickly reduced to Aniline. The best temperature for nitro-compounds is generally between 100° C. and 150° C., when pyrogenous decomposition and reduction of the aromatic nucleus are both completely avoided. High melting solids are best treated by dissolving in a high boiling solvent, such as Amyl alcohol or Cyclohexanol. Thus, α -Nitronaphthalene, dissolved in less than its own weight of Amyl alcohol at 120–130° C., gave α -Naphthylamine, and in the same way, also in Amyl alcohol solution, para-Nitrophenol reduced to para-Amidophenol, and para-Nitroaniline to para-Phenylenediamine.

If alkali is present, the reduction of Nitrobenzene to Aniline is impeded, and a number of intermediate products can be isolated. Thus, Nitrobenzene, in presence of caustic Soda, with Nickel at 100–128° C., gives a considerable yield of Azoxybenzene, $\text{C}_6\text{H}_5\text{-}\overset{\text{O}}{\underset{\text{O}}{\text{N}}}\text{-N-C}_6\text{H}_5$, which can be isolated by removing the Aniline and

unchanged Nitrobenzene in a current of steam. Azoxybenzene in Amyl alcohol solution, and in the absence of alkali, readily reduces to Aniline; but in suspension in dilute aqueous caustic Soda, and with the theoretical proportion of Hydrogen, gives Azobenzene, $\text{C}_6\text{H}_5\text{:N:N-C}_6\text{H}_5$, or, with excess of Hydrogen, Hydrazobenzene,

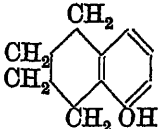
$C_6H_5 \cdot NH \cdot NH \cdot C_6H_5$, which in alkaline solution is reduced to Aniline only slowly.

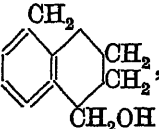
Aminoazobenzene, $NH_2 \cdot C_6H_4 \cdot N \cdot N \cdot C_6H_5$, in Amyl alcohol solution, with Hydrogen and Nickel, like Azobenzene, is easily reduced, giving a mixture of Aniline and para-Phenylenediamine (Brochet, *Bull. Soc. Ind. Mulhouse*, 1922, 11, 703; F.P. 458033).

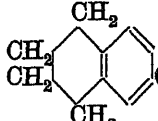
Aromatic substances, with the exception of Phenols and Naphthols, require more energetic hydrogenating conditions. Phenol at the ordinary pressure, in presence of 10 per cent. of active Nickel, commences to absorb Hydrogen at about $50^\circ C.$, giving Cyclohexanol, and the rate of reaction increases rapidly with the temperature up to $150^\circ C.$ To obtain complete hydrogenation within practicable time, however, increased pressure of Hydrogen is necessary, the most satisfactory working conditions being a Hydrogen pressure of 10–20 atmospheres and a temperature between $100^\circ C.$ and $150^\circ C.$ Under these conditions, rapid and quantitative hydrogenation to pure Cyclohexanol occurs, without any production of Cyclohexanone or Cyclohexene, which always form if the temperature is raised to $200^\circ C.$ (*C.R.*, 1922, 175, 583; *Bull. Soc. chim.*, 1922, IV, 31, 1270; U.S.P. 1247629). When a considerable proportion of Nickel is used (5–10 per cent. of the Phenol), the same preparation of catalyst can be used repeatedly before its activity is lost. Brochet employed a type of apparatus that enabled the Cyclohexanol to be discharged from the autoclave through a filter which retained the Nickel, and hydrogenated successively eight charges of Phenol, each of 700 grams, with 40 grams of Nickel, the average rate of absorption of Hydrogen amounting to 400–500 litres daily. The ninth hydrogenation required, however, three days, the catalyst being then very sluggish towards Phenol, but still retaining the power (after washing with alcohol and drying) of reducing Sodium cinnamate. The Cyclohexanol after filtering, and shaking with dilute Caustic soda to remove unchanged Phenol, was almost pure.

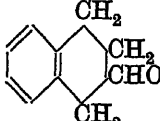
Hydrogenation of ortho-, meta-, and para-Cresols does not commence appreciably below $100^\circ C.$, but at $150^\circ C.$ and a Hydrogen pressure of 10–20 atmospheres proceeds with the same facility as in the case of Phenol, giving quantitatively the corresponding Methyl cyclohexanols.

α - and β -Naphthols, with 12.5 per cent. of their weight of reduced Nickel, at $130^\circ C.$, and Hydrogen at 15 kgm. per sq. cm. are hydrogenated to tetrahydro-derivatives (Brochet and Cornubert, *C.R.*, 1921, 172, 1499; *Bull. Soc. chim.*, 1922, IV, 31, 1280). In each case a mixture of the acyl and aryl tetrahydro-bodies is obtained, the separation being effected by extraction with dilute caustic Soda solution in which the phenolic (aryl tetrahydro) compound is soluble, while the alcoholic (acyl tetrahydro) is not. α -Naphthol gives 15 per cent. of

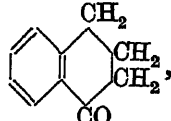
ar.-Tetrahydro- α -naphthol , and 85 per cent. of ac.-

Tetrahydro- α -naphthol, , while β -Naphthol gives 25 per

cent. of ar.-Tetrahydro- β -naphthol, , and 75 per cent.

of ac.-Tetrahydro- β -naphthol, .

The naphthols were also hydrogenated by Schroeter (*Ann.*, 1922, 426, 83; D.R.-P. 352720), who confirmed Brochet's results for β -Naphthol, but proved that, in the case of α -Naphthol, reduction at 200° C. and 10–20 atmospheres Hydrogen pressure, in presence of Nickel, leads to the formation of 10 per cent. of α -Ketotetrahydro-

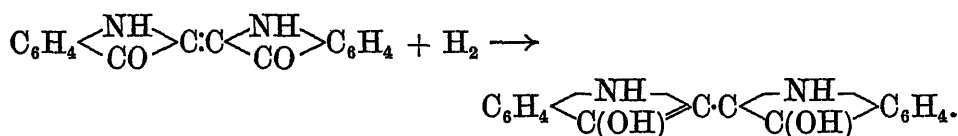
naphthalene, , 25–30 per cent. of ar.-Tetrahydro- α -

naphthol, and a large quantity of Tetrahydronaphthalene. At lower temperatures, the ketone was the main product, and Schroeter regarded it as an intermediate stage in the formation of the other substances.

Phenolic esters and polyphenols are more difficult to hydrogenate than simple phenols, but absorb Hydrogen slowly. Quinol, Resorcinol, Catechol, Pyrogallol, Phloroglucinol, Hydroxyquinol, and 1 : 2 : 4-Trihydroxybenzene were hydrogenated by Sabatier and Aboulenc in the presence of reduced Nickel by the action of Hydrogen under a pressure of 30–50 kgm. per sq. cm., at 115–130° C. in alcoholic solution, or at a slightly higher temperature in water. At 130° C, the corresponding Cyclohexane di- or tri-ol was formed in each case, often in several stereoisomeric forms, but at higher temperatures bye-reactions set in, especially the elimination of hydroxy-groups with formation of Cyclohexanol (*C.R.*, 1921, 173, 1365; 174, 616).

The catalytic method, using Hydrogen at the ordinary pressure,

was also applied by Brochet to the reduction of dyestuffs (especially vats) to the leuco-bases. When Nickel prepared by Sabatier and Senderens' method is added to a suspension of Indigotin in water, the mixture agitated, and Hydrogen passed, reduction to Indigo-white slowly occurs:

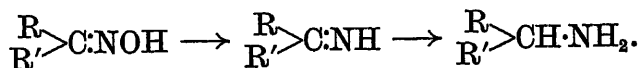


In presence of alkali, the reduction is much quicker, and also increases in speed as the temperature is raised or if Hydrogen under pressure is used. At the optimum temperature, 45–60° C., 40 grams of Indigotin and 20 grams of Nickel, suspended in 170 c.c. of water and 25 c.c. of caustic Soda solution (36° Bé.) absorb the theoretical proportion of Hydrogen in 30–40 minutes, giving a solution of Leuco-indigo more concentrated than is obtained by the ordinary chemical methods of reduction, and free from inorganic salts. The Nickel is easily recovered by filtration, and is active indefinitely (F.P. 473536; E.P.s. 16936 of 1913; 19848 of 1914; U.S.P. 1247927; C.R. 1915, 160, 306; *Bull. Soc. chim.*, 1915, 17, 124; *Rev. Gén. Mat. Col.*, 1922, 27, 131). Other dyes, such as Thioindigo, Indanthrene, Algol, Ciba, Helindone, and Hydron colours, are also reduced, as well as simple Anthraquinone derivatives like Quinizarine (which involves complications by the chemical methods) and Triphenyl methane and Azo-colours, which are not reoxidised by air, such as Malachite-green.

Boehringer und Söhne have patented the hydrogenation, in aqueous suspension or solution, in presence of Nickel suboxide, of Quinine, Morphine, Cinnamyl-cocaine, and Cinnamic acid, to dihydro-derivatives, and of Amino acetonitrile, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CN}$, to Ethylene diamine (E.P. 21883 of 1914; D.R.-PP. 306939, 307894). Methyl or Ethyl alcohol as solvent instead of water is claimed as an improvement in E.P. 21948 of 1914.

Acetylenic compounds of the type $\text{RR}'\cdot\text{C(OH)}\text{C}:\text{CH}$ made by Locquin and Wouseng by condensing ketones $\text{R}\cdot\text{CO}\cdot\text{R}'$ with Acetylene, have been hydrogenated by Brochet's method. Palladium and Platinum catalysts caused a cleavage of the molecule, regenerating the original ketone, but Nickel (10 per cent. by weight of the compounds to be reduced), using a Methyl alcohol solution, induced rapid hydrogenation, with evolution of heat. By stopping the hydrogenation at the right stage, tertiary ethylenic alcohols were obtained intermediately, in high yields, the following being prepared in this way: Methyl isohexyl vinyl carbinol, Diphenyl vinyl carbinol, and Methyl isobutyl vinyl carbinol (C.R., 1922, 174, 1551).

Mignonac has shown that when ketoximes are reduced by Brochet's method, ketimines are formed, which further reduce to amines,



The oximes were dissolved in absolute Alcohol in which finely-divided Nickel, prepared by reduction of the oxide at 300° C., was suspended, and the theoretical amount of Hydrogen at the ordinary pressure passed into the strongly agitated suspension. When the requisite Hydrogen had been absorbed, the catalyst was separated by filtration, the product obtained by fractional distillation under reduced pressure, and dried over Phosphoric anhydride *in vacuo*.

Acetophenone oxime gave Methyl phenyl ketimine, $\text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{CH}_3 \cdot \text{NH}$, and Propiophenone oxime, $\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \\ \text{C:NOH} \\ \diagdown \\ \text{C}_6\text{H}_5 \end{array}$, gave Ethyl phenyl ketimine, $\text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{C}_2\text{H}_5 \cdot \text{NH}$, isolated as the hydrochlorides.

Benzophenone oxime, $(\text{C}_6\text{H}_5)_2\text{C:NOH}$, in the same way yielded Diphenyl ketimine, $(\text{C}_6\text{H}_5)_2\text{C:NH}$, while Phenyl α -naphthyl ketimine was obtained almost quantitatively from its corresponding oxime. The stability of the ketimines, especially the resistance of the $\cdot\text{NH}$ group to hydrolysis by water, much increased in the order in which the examples are given: the more complicated radicals, especially the strongly electronegative ones, exerting a stabilising influence.

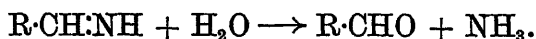
Cyclohexanone oxime gave mostly Cyclohexanone, and the Cyclohexyl ketimine, $\text{C}_6\text{H}_{10} \cdot \text{N} \cdot \text{C}_6\text{H}_{11}$, when treated in this way (*C.R.*, 1920, 170, 936).

By the hydrogenation of nitriles, *e.g.*, Benzonitrile, $\text{C}_6\text{H}_5 \cdot \text{CN}$, Mignonac was unable to obtain the simple imines, $\text{C}_6\text{H}_5 \cdot \text{CH:NH}$, these immediately undergoing further changes.

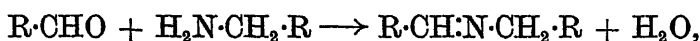
The reduction of Benzonitrile in contact with Palladium is well known to produce a mixture of the Benzylamines and Benzaldehyde (*Ber.*, 1908, 42, 1554). Adopting the procedure used in the case of the oximes, with a Nickel catalyst, Mignonac found that Benzonitrile absorbed Hydrogen regularly and rapidly, and Ammonia was formed. When a certain proportion of Hydrogen had been taken up, the product contained 1 part of Benzylamine and $2\frac{1}{2}$ parts of Benzylidene benzylimine, $\text{C}_6\text{H}_5 \cdot \text{CH:N} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5$. Continuation of hydrogenation reduced the latter to Dibenzylamine. *ortho*-Toluonitrile, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CN}$, on reduction in the same way gave *ortho*-Tolylamine, $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NH}_2$, and *ortho*-Methyl benzylidene *ortho*-methyl benzylamine, and *para*-Toluonitrile gave analogous products. Mignonac regarded the aldimine, $\text{C}_6\text{H}_5 \cdot \text{CH:NH}$, as a probable intermediate product, but was unable to control the reaction and isolate it (*C.R.*, 1920, 171, 114).

The mechanism of the hydrogenation of nitriles in aqueous-

alcoholic solution in presence of Acetic acid has been elucidated by Rupe and Glenz (*Helv. Chim. Acta*, 1922, 5, 937) and Rupe and Hodel (*ibid.*, 1923, 6, 865). The hydrogenation of Valero-nitrile, $C_5H_{11} \cdot CN$, Phenyl acetonitrile, $C_6H_5 \cdot CH_2 \cdot CN$, β -Phenyl propionitrile, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CN$, and Benzonitrile, $C_6H_5 \cdot CN$, using a large proportion of catalyst (about twice the weight of nitrile), gave as the main product the corresponding secondary amines. The first product was the aldimine, $R \cdot CH:NH$, part of which further reduced to primary amine, $R \cdot CH_2 \cdot NH_2$, the remainder hydrolysing to aldehyde and Ammonia,



The aldehyde then condensed with the primary amine to form a Schiff's base,

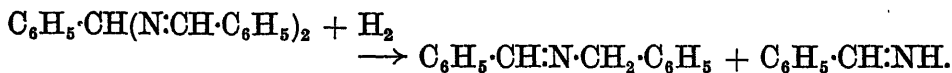


which, as shown by Mailhe (see later), is readily hydrogenated to secondary amine,

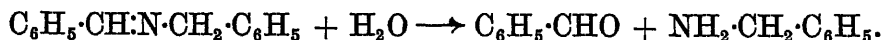


The relative proportions of primary and secondary amines formed will therefore depend upon the ease with which the aldimine is hydrolysed: conditions which retard this (such as limitation of the quantity of water present) conducing to greater formation of the primary amine.

Mignonac had developed a general method of preparation of amines from aldehydes and ketones by catalytic reduction by Brochet's method (*C.R.*, 1920, 171, 1148; 1921, 172, 223). When Hydrobenzamide (from Benzaldehyde and Ammonia), either in the pure state or in absolute Alcohol solution, is shaken in an atmosphere of Hydrogen in presence of finely-divided Nickel, Benzylamine is formed. The first action is probably a scission of the molecule, with the formation of Benzyl benzylidene amine and Benzylidine imine:



To prepare Benzylamine, the Hydrobenzamide is best hydrogenated at 15–18° C. without a solvent. Four atomic equivalents of Hydrogen are taken up, and the Benzyl benzylidene amine in the product is then hydrolysed with dilute mineral acid to Benzylamine and Benzaldehyde, which latter can be utilised for more Hydrobenzamide:



The procedure was made of general application by adding to a 7–8 per cent. solution of Ammonia in absolute Alcohol a molecular

equivalent of aldehyde or ketone, and reducing by shaking with Hydrogen at the ordinary temperature and pressure in presence of Nickel. Absorption of gas was regular until hydrogenation was complete, when the catalyst was removed by filtration and the amine isolated. From the appropriate aldehydes the following amines were made. Ethyl, Diethyl, Butyl, Dibutyl, Heptyl, Benzyl, and para-Ethylbenzyl: and from suitable ketones the following: isoPropyl, Di-isopropyl, Octyl, Cyclohexyl, α -Phenyl ethyl, α -Phenyl propyl.

The hydrogenation of certain classes of substances, which, in the gaseous phase, is difficult on account of unfavourable physical properties, can often be carried out with great ease in liquid media. For example, Mailhe has developed a general method of preparation of secondary amines by hydrogenation of Schiff's bases. In the gaseous state this reaction is inconvenient and slow, even at 220° C., on account of the low volatility of Schiff's bases, and accompanied by destruction, hence inferior yields, an impure product, and a catalyst quickly poisoned by a non-volatile deposit. Mailhe avoided these difficulties by effecting the fixation of Hydrogen to the liquid base at 170° C., violently agitating the liquid in presence of catalytic Nickel in a current of Hydrogen (*C.R.*, 1921, 172, 280; *Bull. Soc. chim.*, 1921, [4], 29, 106). Excellent yields of secondary amine, without by-products, were obtained in all cases, the reaction being very rapid. The following Schiff's bases were hydrogenated in this way: the Benzylidene derivatives of Aniline, ortho-, meta-, and para-Toluidine, and para-Anisidine.

Kelber has shown that catalytic reduction extracts halogens from organic combination sufficiently rapidly and completely to serve as a basis for their estimation. The substance is dissolved or suspended in water, or aqueous alcohol, rendered alkaline, a suitable quantity of Nickel catalyst (prepared by reducing basic Nickel carbonate in Hydrogen at 310–320° C.) added, and the whole shaken with Hydrogen, when the halogen is gradually replaced (*Ber.*, 1917, 50, 305). Busch and Stöve had already proposed palladised Calcium carbonate for the same purpose, using strongly alkaline aqueous or alcoholic media, but the method was of very limited application owing to the facility with which the catalyst was poisoned (*Ber.*, 1916, 49, 1063).

A general method for the preparation of aldehydes by catalytic reduction of acid chlorides has been worked out by Rosenmund and Zettsche (*Ber.*, 1918, 51, 585, 594). The acid chloride is dissolved in 3 to 5 times its volume of dry Xylene or Cymene, catalyst added, and the solution boiled under a reflux condenser, meanwhile passing gaseous Hydrogen. The most satisfactory catalysts are palladised Barium sulphate containing 5 per cent. of the metal, or Nickel, made in the way recommended by Kelber for the extraction of halogens.

Reduction is rapid, as indicated by the evolution of Hydrochloric acid, and when complete the aldehyde is isolated by distillation, or shaking with Sodium bisulphite, when the bisulphite compound separates. The reaction is not suppressed even by small quantities of Phosphoryl chloride, which may be present in the acid chloride, but the action is capricious, as stated by Abel and by Schlievinsky, and admitted by Rosenmund, who showed that certain foreign materials were necessary (see page 30). In a later paper, addition of partial poisons was recommended, especially Quinoline, or sulphurised Quinoline. Under satisfactory conditions the yields were good and the method may be regarded as one of the most convenient for preparation of certain aldehydes. It is of general application for the preparation of either aliphatic or aromatic aldehydes, unsaturated aldehydes (from unsaturated acid chlorides) or di-aldehydes (from the chlorides of dicarboxylic acids). The following have been made: Benzaldehyde (yield 97 per cent.), ortho-Chlorobenzaldehyde, para-Nitrobenzaldehyde, Phenyl acetaldehyde (*Ber.*, 1921, 54 B, 425, 638, 1092), Butyraldehyde (yield 50 per cent.), Stearaldehyde, para-Methyl carbonatobenzaldehyde, $C_6H_4 \begin{smallmatrix} \text{CHO} \\ \text{O} \cdot \text{CO}_2 \cdot \text{CH}_3 \end{smallmatrix}$, 3 : 4 : 5-Trimethyl carbonatobenzaldehyde, $\text{CHO} \cdot C_6H_4 (\text{O} \cdot \text{CO}_2 \cdot \text{CH}_3)_3$, 3 : 4 : 5-Triacetoxy-benzaldehyde (*Ber.*, 1918, 51, 594), Gallaldehyde (3 : 4 : 5-trihydroxy-benzaldehyde) (*Ber.*, 1922, 55 B, 2357). Sebacic dialdehyde, $C_8H_{16}(\text{CHO})_2$ (80 per cent. yield, using Sebacyl chloride in Xylene solution at 150° C., palladised kieselguhr, and sulphurised Quinoline, *Ber.*, 1922, 55 B, 609), Suberyl, isoPhthalyl, and Terephthalyl aldehydes (*Ber.*, 1921, 54 B, 2888), Vanillin (85.5 per cent. yield), Phenoxyacetaldehyde (72 per cent. yield), Anisaldehyde (81 per cent. yield), Cinnamaldehyde (60 per cent. yield), ortho-Chlorocinnamaldehyde (*Ber.*, 1923, 56 B, 1481).

The rate of hydrogenation of unsaturated substances in the liquid phase in presence of Nickel has been studied by Armstrong and Hilditch (*Proc. R.S.*, 1921, 100A, 240). Ethyl cinnamate, Ethyl linoleate, and Pinene were shown to absorb Hydrogen at a rate proportional to its pressure, when as much as 0.1 per cent. of Nickel was present. They regarded this as indicating that the Hydrogen reacted in the molecular rather than in the atomic form, since in the latter case the rate of hydrogenation would vary as the square root of the concentration. In the case of Linoleic and Linolenic acids and Citral, however, the rate of hydrogenation was less than proportional to the pressure, when 0.01 to 0.02 per cent. of Nickel was present, and the abnormality was most marked in the multi-ethylenic compound. Armstrong and Hilditch regarded this as further evidence in favour of their view that during hydrogenation some of the Nickel becomes chemically associated with the unsaturated substance. This evidence would, however, seem to be compromised by the

observation that in the case of some substances, *e.g.*, Geraniol, Terpeneol, Oleic acid, the rate of hydrogenation increased at a rate greater than the rate of increase of pressure.

Schroeter's Researches

In a remarkable investigation exploring the whole field of Tetrahydronaphthalene derivatives, Schroeter and his co-workers developed the catalytic method, first, to preparation of large quantities of Tetrahydronaphthalene and, secondly, to the fractional reduction of mixtures of isomeric nitro-derivatives (*Ann.*, 1922, 426, 1, 17, 83; E.P.s. 147446, 147474, 147476, 147488, 147580, 147747 of 1920). The best method of preparation of Tetrahydronaphthalene is as follows:—

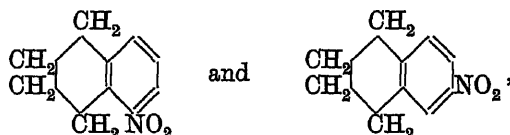
Purification of Naphthalene. Substances anticatalytic towards Nickel can be eliminated from Naphthalene by heating with an easily fusible or finely-divided metal, such as Sodium, Potassium, Copper, Iron, Nickel, or such reactive agents as Sodamide or Calcium carbide. When the Naphthalene is purified in this way, and then vacuum distilled, the same specimen of Nickel can be used for hydrogenation many times without appreciable loss of catalytic activity. A similar process of purification is recommended in D.R.-PP. 324862 and 324863 of the Tetralin Gesellschaft, while D.R.-P. 324861, by the same firm, recommends stirring of the Naphthalene in the fused state with finely-divided porous materials, such as fuller's earth, kieselguhr, or animal charcoal, until it no longer shows a red colour with strong Sulphuric acid, even on standing.

Hydrogenation. In a 4-litre autoclave fitted with an agitator, cooled packing box, thermometer tube, pressure gauge, and gas inlet are placed 512 grams (4 gram-molecules) of purified Naphthalene, and 15–20 grams of active Nickel catalyst. When the autoclave is tight, the Naphthalene is melted and pure Hydrogen injected to a pressure of 12–15 atmospheres. The temperature is then raised to 180–200° C., stirring meanwhile, using an oil bath or bare flame. At this temperature the pressure begins to fall, and falls rapidly in 45–60 seconds by about 1 atmosphere. When the pressure has fallen to 8 to 5 atmospheres, more Hydrogen is added to restore the original pressure, and so on until the total pressure reduction corresponds with an absorption of 8 molecular equivalents (= 178 litres at 0° C. and 760 mm.). The pressure gauge indicates when this point has been reached, since the rate of absorption abruptly diminishes. This requires about 1 to 1½ hours. When the hydrogenation is completed the delivery tube is connected to a condenser, the excess Hydrogen released and the Tetrahydronaphthalene distilled off under diminished pressure. This requires about 25 minutes. The autoclave is then closed, leaving a slightly reduced pressure within, while the delivery tube is dipped beneath the surface of molten Naph-

thalene, and the entry valve opened. The autoclave is thereby recharged so that within two hours of commencing the first hydrogenation the second can be started. The second hydrogenation is usually faster than the first owing to the Nickel increasing in activity with use. Hydrogenation can be discontinued and restarted at any stage, and after 25 operations, carried out without opening the autoclave, the catalyst is nearly as active as initially.

Tetrahydronaphthalene made in the way described is a clear, colourless liquid, of specific gravity 0.974 to 0.976, freezing at -27° to -30° C., and boiling at $206-208^{\circ}$ C. It is stable in light and air at ordinary temperatures, but when the hot vapour of Tetrahydronaphthalene is brought into contact with dry air, water vapour is formed, this probably arising from the partial oxidation of the hydroaromatic ring forming Dihydronaphthalene. Tetrahydronaphthalene has assumed considerable technical importance by virtue of its strong solvent action on fats, oils, resins, Sulphur, Naphthalene, Anthracene, and numerous other substances.

Fractional Reduction of the Nitrotetrahydronaphthalenes. When Tetrahydronaphthalene is nitrated at $0-5^{\circ}$ C. by brisk agitation with a nitrating mixture of Nitric and Sulphuric acids containing only a small excess of the former, a mixture of the two isomeric α - and β -Nitrotetrahydronaphthalenes,



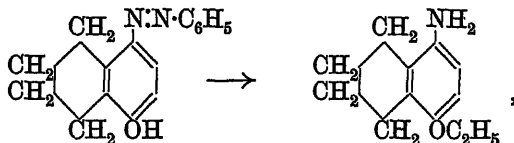
is obtained. Various methods of separation of these isomers are available, the most interesting depending upon the different conditions necessary for their reductions to amines, the α -nitro-body resisting reduction considerably more strongly than the β .

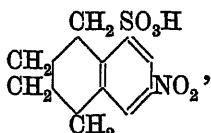
A mixture of the two Nitrotetrahydronaphthalenes (177 grams = 1 gram-molecule), carefully purified by distillation *in vacuo*, is dissolved in 90-100 grams of Tetrahydronaphthalene, catalytic Nickel added, and reduced with compressed Hydrogen in an agitator autoclave. Gas absorption commences at $90-110^{\circ}$ C., and the temperature is very gradually raised from this point until about 40 litres of Hydrogen have been absorbed. The reduction is then stopped, the solution filtered from catalyst, and agitated with warm concentrated Hydrochloric acid. The residual oil is then distilled under reduced pressure, collecting the solvent and the nitro-body separately. The latter crystallises on standing and is almost pure α -Nitro-tetrahydronaphthalene, melting point 34° C., boiling point 157° C. at 13 mm. pressure. It can be completely purified by recrystallisation from Methyl alcohol.

The Hydrochloric acid solution contains β -Amido-tetrahydronaphthalene, which easily crystallises as the pure hydrochloride on cooling. A nearly complete separation can be obtained by "salting out."

More prolonged reduction of the mixture of nitro-bodies, or less careful temperature regulation of the reaction, results in complete reduction to a mixture of the two Amido-tetrahydronaphthalenes, thus: Freshly-distilled Nitrotetrahydronaphthalene mixture (1062 grams) is introduced into a mixture of 400 c.c. of Tetrahydronaphthalene and 30 grams of catalyst in an agitator autoclave, Hydrogen admitted to a pressure of 10 to 12 atmospheres and the autoclave heated. Reduction begins at about 100°C ., and at 120°C . proceeds rapidly under its own heat, so that it is complete within 2 hours.

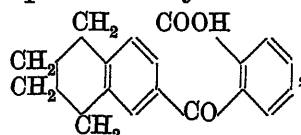
Other derivatives of Tetrahydronaphthalene, such as dinitro-compounds, Nitro-sulphonic acids, and azo-compounds, were similarly reduced by Schroeter. As examples may be mentioned 1:3-Dinitro-2-methoxy-tetrahydronaphthalene, which gave the corresponding diamine; 4-Benzene-azo-tetrahydro- α -naphthol, which on ethylation with Ethyl bromide and alcoholic caustic Potash and subsequent catalytic reduction gave para-Amino tetrahydronaphthyl ethyl ether,



and 2-Nitrotetrahydronaphthalene 4-sulphonic acid, ,

which, in the form of its Sodium salt, easily reduced as follows: 5 grams were dissolved in 50 c.c. of water, mixed with finely-divided Nickel, and enclosed with Hydrogen at 16 to 20 atmospheres in an autoclave. At 180°C . reduction was very rapid, the theoretical volume of Hydrogen being absorbed, and 2-Amidotetrahydronaphthalene 4-sulphonic acid quantitatively produced.

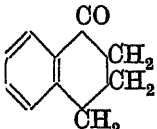
Tetrahydronaphthalene and Phthalic anhydride in Benzene solution undergo the usual condensation when heated in presence of Aluminium chloride, and a 90 per cent. yield of Tetrahydro

β -naphthoyl-ortho-benzoic acid, , is formed.

This is easily reduced by Zinc and acid to the Tetrahydro β -naphthyl-ortho-benzoic acid, which in turn is hydrogenated in

contact with Nickel at 180–200° C. to a perhydro-derivative, whose Sodium salt possesses soapy properties (Schroeter, *Ber.*, 1921, 54 B, 2242).

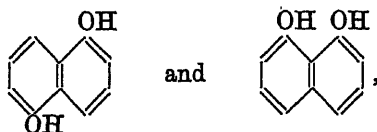
Schroeter also hydrogenated the naphthols and certain of their derivatives. α -Naphthol was mixed with Tetrahydronaphthalene and catalyst, consisting of Nickel mounted upon kieselguhr, and subjected to hydrogenation at 10–20 atmospheres pressure and 120–180° C. After absorption of about 3 atomic equivalents of Hydrogen, the reduction was finished, and the product fractionated under reduced pressure. The product boiling at 134–135° C. at 14 millimetres

was α -Keto-tetrahydronaphthalene, , while the higher-

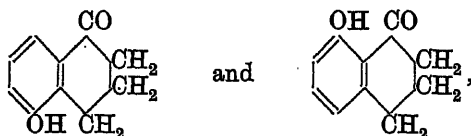
boiling portion consisted of unchanged α -Naphthol, and ar.-tetrahydro α -Naphthol.

β -Naphthol similarly heated gave no ketone, being mainly hydrogenated to ac.-Tetrahydro β -naphthol with a small quantity of ar.-Tetrahydro β -naphthol (cf. Brochet, also D.R.-P. 352720; *Ann.*, 1922, 426, 83).

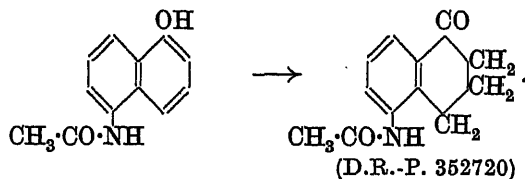
The 1 : 5- and 1 : 8-Dihydroxy naphthalenes,



hydrogenated in the same way, gave respectively 1-Keto-5-hydroxy- and 1-Keto-8-hydroxy-tetrahydronaphthalenes,



while 1-Hydroxy-5-acetylamino-naphthalene gave 1-Keto-5-acetylaminotetrahydronaphthalene,



Schroeter also hydrogenated Anthracene and Phenanthrene in the same way as Naphthalene (D.R.-PP. 352721 and 352719). The hydrocarbon purified by contact with a heated finely-divided or molten metal was dissolved in Tetrahydronaphthalene and treated with

Hydrogen at 15 atmospheres pressure at 180–220° C. in presence of catalytic Nickel deposited upon kieselguhr or fuller's earth. Four molecular equivalents of Hydrogen were quickly absorbed in each case, and the products isolated by fractionation under diminished pressure were the symmetrical octahydro-derivatives, Octahydro-

anthracene ("Oethracene"), $C_6H_8 \begin{smallmatrix} \diagup CH \\ \diagdown CH \end{smallmatrix} C_6H_8$, and Octahydrophen-

anthrene ("Octanthrene"), $C_6H_8 \begin{smallmatrix} \cdot CH \\ \cdot CH \end{smallmatrix}$, respectively, these constitu-

tions being established by independent syntheses. Schroeter's method of hydrogenation is particularly suited for large-scale laboratory preparations or manufacturing processes, and Tetrahydronaphthalene is now made on a considerable scale. Von Braun and various collaborators have investigated by this method the conditions for preparation of a number of other hydrogenated products. Employing an autoclave fitted with a mechanical stirrer, a Nickel catalyst and Hydrogen under 10–15 atmospheres pressure, the following hydrogenations were effected:—

Indene at 200° C. gave very easily a theoretical yield of Hydrindene. Acenaphthene, purified by a single recrystallisation from alcohol, at 210° C. gave rapidly and quantitatively Tetrahydroacenaphthene (*Ber.*, 1922, 55 B, 1680). Phenetidine, $C_2H_5O \cdot C_6H_4 \cdot NH_2$, at 210–230° C. and Hydrogen at 6–7 atmospheres, preferably in Tetrahydronaphthalene solution, gave a mixture of two stereoisomeric para-Diethoxyhexahydrodiphenylamines,



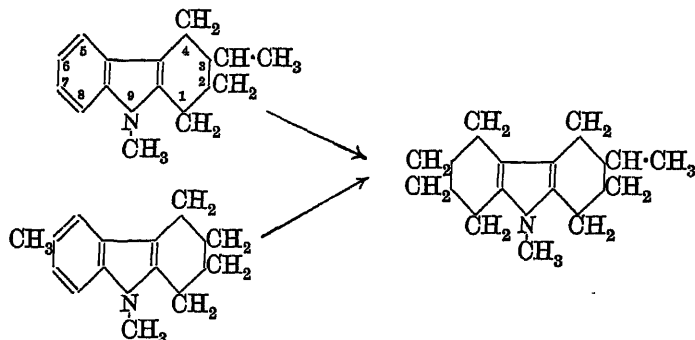
(*Ber.*, 1922, 55 B, 3770). 2:2'-Dihydroxy-diphenyl at 230° C. undergoes at the same time hydrogenation and internal condensation, with formation of an oxide ring. The product, Hexahydro-di-

phenylene oxide, $C_6H_{10} \begin{smallmatrix} \diagup O \\ \diagdown \end{smallmatrix} C_6H_4$, was very stable towards further reduc-

tion, but was easily oxidised (*Ber.*, 1922, 55 B, 3761). Pyrazole, in spite of elaborate purification, resisted hydrogenation, even at 260° C. and 30 atmospheres pressure of Hydrogen, an unexpected behaviour suggesting the presence of an anticatalyst very difficult to eliminate. *n*-Alkyl carbazoles easily hydrogenated, with initial addition of 4 atoms of Hydrogen to one benzene nucleus, forming tetrahydro-derivatives. Continuing the action, the second Benzene nucleus was hydrogenated, and an octahydro-derivative formed, but the reaction was not a clean one. Thus, at 210–215° C. and 25 atmospheres, 9-Methyl carbazole, after absorbing about 7 atomic proportions of Hydrogen, still was largely unchanged, some was perhydrogenated with loss of Ammonia, while the remainder was

converted into a mixture of the tetrahydro- and octahydro-derivatives. Ethyl carbazole behaved similarly (*Ber.*, 1922, 55 B, 3792).

The two tetrahydro-derivatives, 6:9-Dimethyl and 3:9-Dimethyl 1:2:3:4-tetrahydro carbazoles, were hydrogenated, and gave identical Dimethyl octahydro carbazoles, proving that the hydrogenated substances were octahydro carbazoles, and not reduced bodies formed by ring scission,



(*Ber.*, 1925, 58 B, 2156.)

Von Braun, Petzold, and Seemann showed that the Schroeter procedure was a most satisfactory one for obtaining Tetrahydroquinoline and its derivatives. At 210–215° C. a quantitative yield

of 1:2:3:4-Tetrahydroquinoline, was obtained from

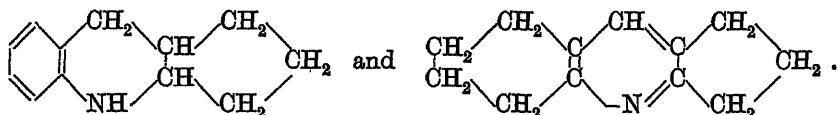
Quinoline. At higher temperatures, some decahydro-body was formed, and reduction in part to tertiary bases of the Pyridine series also occurred (*Ber.*, 1922, 55 B, 3779). By hydrogenating a large number of Quinoline derivatives, it was shown that when substituents were present in the benzenoid nucleus, or in position 2, the homologue behaved on hydrogenation like the parent base, and gave almost exclusively the 1:2:3:4-tetrahydro-derivative. Substituents in positions 3 or 4, however, influenced the hydrogenation in such a way that the benzenoid nucleus was hydrogenated, and a mixture of two tetrahydro-bodies, the relative proportions depending on the particular substituents used, was formed. These conclusions were based on the following hydrogenations:

The 6-Methyl, 6-Chloro, 6:7-Ethylene dioxy and the 2-Phenyl derivatives of Quinoline all gave exclusively the 1:2:3:4-tetrahydro-derivatives. On the other hand, 3-Ethyl quinoline (at 180–190° C.) and 3-Phenyl quinoline (very easily at 160° C.) gave mixtures of the corresponding 1:2:3:4- and 5:6:7:8-tetrahydro-derivatives; while 3-*n*-Amyl quinoline gave the two tetrahydro-derivatives in approximately equal quantities. Neither the speed

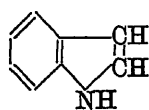
of hydrogenation nor the proportion of the products was much influenced whether the pure base was used, or a Tetrahydronaphthalene solution. A systematic study of hydrogenation of the Methyl quinolines (*Ber.*, 1923, 56 B, 1338) further illustrated these general rules.

A methyl group in position 5, 6, 7, or 8 caused hydrogenation to occur exclusively in the Pyridine nucleus, yielding 1 : 2 : 3 : 4-tetrahydro-bases. 2-Methyl quinoline gave a mixture of 96 per cent. of 1 : 2 : 3 : 4- and 4 per cent. of 5 : 6 : 7 : 8-tetrahydro-2-Methyl quinoline. The 3- and 4-Methyl quinolines, however, gave much greater relative proportions of hydrogenation in the benzenoid ring, the quantities being 33 per cent. of 5 : 6 : 7 : 8- and 66 per cent. of 1 : 2 : 3 : 4-tetrahydro-derivatives. More methyl groups introduced into the Pyridine nucleus of the molecule further increased the hydrogenation in the benzenoid nucleus, as, for example, with the 2 : 3- and 2 : 4-Dimethyl quinolines, which gave mainly Dimethyl 5 : 6 : 7 : 8-tetrahydroquinolines. The same tendency was produced when the two substituents in the Pyridine nucleus took the form of a third ring (*Ber.*, 1923, 56 B, 1347). Thus, Tetrahydroacridine (made from Isatin and Cyclohexanone) at 150° C. easily hydrogenated, giving a mixture of the two octahydro-derivatives, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \end{smallmatrix} C_6H_{10}$

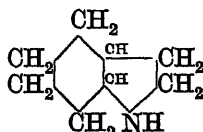
and $C_6H_5 \begin{smallmatrix} \text{CH} \\ \text{N} \end{smallmatrix} C_6H_5$; and 2 : 3-Trimethylene quinoline (from Isatin and Cyclopentanone) at 170° C. hydrogenated to a mixture of



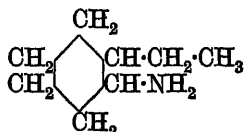
The hydrogenation of Indole and its derivatives which occurs at 220–250° C. follows the same general rules as in the case of Quinoline, Hydrogen first entering the heterocyclic ring. The presence of substituents in this ring increases its resistance towards hydrogenation, with the result that more or less hydrogenation of the benzenoid nucleus occurs. The main difference between the hydrogenated Indoles and Quinolines arises from the greater instability of the former, the pyrrolidine ring tending comparatively easily to open with formation of Ammonia and alkylated anilines and Cyclohexylamines :



Indole.



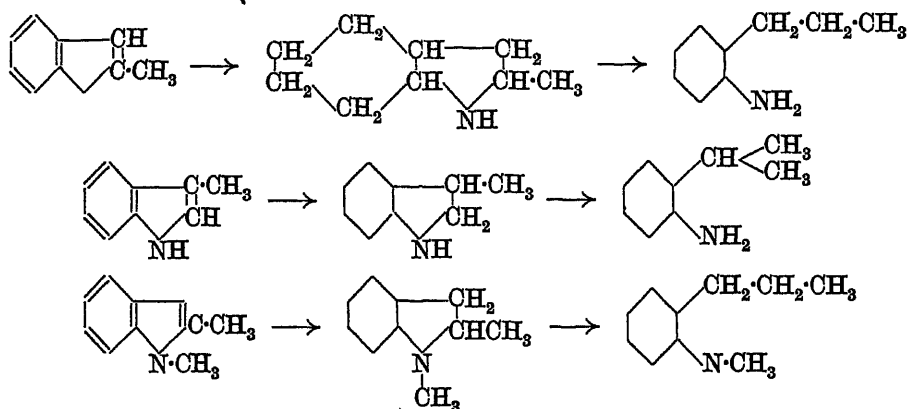
Octahydrindole.



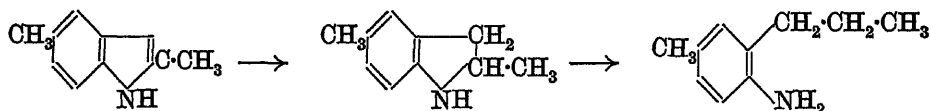
o-Ethylcyclohexylamine.

(*Ber.*, 1924, 57 B, 392; 1925, 58 B, 385, 387).

Indole, when exhaustively hydrogenated in contact with Nickel at 225° C., yields 8 per cent. of unchanged base and 66 per cent. of a basic substance finally proved to consist mainly of ortho-Ethylcyclohexylamine, while the remainder suffers decomposition with formation of Ammonia. A methyl group in close proximity with the Nitrogen atom stabilises the pyrrolidine ring, with the result that 2-Methyl and 3-Methyl and 1:2-Dimethyl indoles at 220° C. give largely the corresponding Methyl octahydrindoles, together with varying quantities of the Methyl 4:5:6:7-tetrahydrindoles. At 240–250° C., however, the heterocyclic ring opens, and the main products are respectively ortho-Propyl cyclohexylamine, ortho-isoPropyl cyclohexylamine, and ortho-Propyl hexahydromethylaniline:—



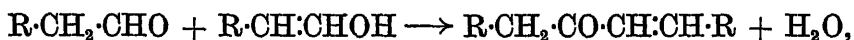
2:5-Dimethyl indole is much more difficult to hydrogenate, and at 250° C. gives very little 2:5-Dimethyl octahydrindole, the greater quantity reducing by opening of the ring to ortho-Propyl para-toluidine:—



2:4:7-Trimethyl indole similarly gives 2-Propyl 3:6-xylidine, and 3-Ethyl indole at 235° C. gives ortho-isoButyl cyclohexylamine, but 1-n-Butyl indole gives 1-n-Butyl octahydrindole, with a little ortho-Ethyl cyclohexylamine.

Aldehydes and Ketones. Von Braun and collaborators found that aliphatic or aromatic ketones and aromatic aldehydes, when submitted to hydrogenation by his procedure, gave smoothly the corresponding secondary or primary alcohols, respectively. When, however, the aldehydic group was attached to an aliphatic side-chain, or when aliphatic aldehydes were reduced, then in addition to the corresponding primary alcohols there was always obtained a certain amount of secondary alcohol, arising from the doubling of the carbon

chain. This was attributed to condensation between an enolised and an unchanged Aldehyde molecule,



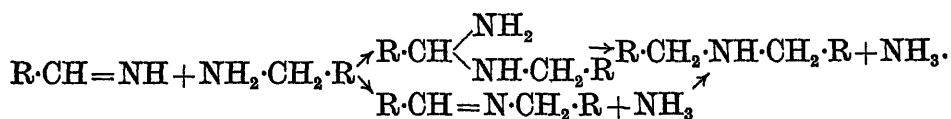
and subsequent reduction of the unsaturated ketone so formed. The formation of high-boiling bye-products observed by previous investigators is therefore explained (*Ber.*, 1923, 56 B, 2172). These conclusions were reached from the following reductions :—

Styryl methyl ketone gave almost quantitatively β -Phenyl methyl carbinol, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CHO H \cdot CH_3$. Acetophenone could not be completely reduced, and gave a certain proportion of unchanged ketone along with Phenyl methyl carbinol. Benzaldehyde, and ortho-Aminobenzaldehyde in Decahydronaphthalene solution, gave almost quantitatively the corresponding alcohols. Cinnamaldehyde, on the other hand, gave a mixture of Phenyl-propyl alcohol, the normal product, and the secondary alcohol, Phenylethyl-phenylpropyl carbinol, $C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CHO H \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C_6H_5$. Hydrocinnamaldehyde gave the same mixture. Phenyl acetaldehyde in the same way gave a mixture of Phenyl ethyl alcohol and Phenylethyl benzyl carbinol, $C_6H_5 \cdot CH_2 \cdot CHO H \cdot CH_2 \cdot CH_2 \cdot C_6H_5$; Heptaldehyde at 140–150° C. gave Heptyl alcohol and Hexyl heptyl carbinol,



and Dipropenyl glycol a mixture of stereoisomeric Octane diols.

Nitriles. Von Braun, Blessing and Zobel (*Ber.*, 1923, 56 B, 1988) showed that except in the case of the simpler aliphatic members (in presence of which a Nickel catalyst becomes poisoned), nitriles reduced rapidly and smoothly to primary and secondary amines, in yields approaching the quantitative. Tertiary amines were not formed. Alterations of Hydrogen pressure exerted little effect on the course of the reaction, and the influence of temperature was variable, but likewise not very marked. The effects of a solvent and concentration of nitrile in the solvent, on the other hand, were very great, increase of concentration in all cases much favouring the formation of primary base. Alcoholic solvents, especially Cyclohexanol and Benzyl alcohol, at the same time tended to condense with the amine, giving varying quantities of Cyclohexylamine or Benzylamine derivatives, respectively. The first reduction product was assumed to be the aldimine, $R \cdot CH : NH$, which then either reduced to primary amine or reacted with primary amine as follows :—



In the following reductions the temperature was maintained at 110–130° C. until Hydrogen ceased to be absorbed. Acetonitrile and Propionitrile were only slightly hydrogenated. *n*-Octonitrile and γ -Phenoxy *n*-butyronitrile gave high yields of the primary and secondary Octylamines and δ -Phenoxy *n*-butylamines. Benzonitrile gave Benzylamine and Dibenzylamine: a very advantageous mode of making the former when Amyl alcohol or Decahydronaphthalene was used as solvent. With Cyclohexanol as solvent, Cyclohexyl benzylamine also was formed.

α - and β -Naphthonitriles at 190° C. gave mainly the primary amines, α - and β -Naphthyl methylamines, $C_{10}H_7 \cdot CH_2 \cdot NH_2$, the naphthalene nucleus, contrary to expectations, not being hydrogenated under these conditions. Phenyl acetonitrile gave β -Phenylethylamine and the secondary amine, and, in presence of Cyclohexanol as solvent, β -Phenylethyl-cyclohexylamine in addition. β -Phenylpropionitrile, dissolved in Decahydronaphthalene, or β -Phenyl ethyl alcohol, hydrogenated to γ -Phenyl-propylamine, and the corresponding secondary base, and in presence of Benzyl alcohol as solvent, gave also the derived Benzyl-amines. Ortho-, meta-, and para-Toluenitriles gave the corresponding primary and secondary Xylylamines, while α - and β -Tetrahydronaphthonitriles in Tetrahydronaphthalene solution gave a mixture of the corresponding primary and secondary ar.-Tetrahydronaphthyl-methylamines, $C_{10}H_{11} \cdot CH_2 \cdot NH_2$, the β -compound producing a larger proportion of the secondary and a lower proportion of the primary than the α -compound.

Hydrogenation of Oils

For many years the production of solid fats from liquid oils has been a technical problem of outstanding importance, on account of the wide applicability of the former and the superabundant supply of the latter. In its chemical aspect the problem consists simply in the reduction of an ethylenic linkage, converting an unsaturated fatty acid, or its glyceride, into the corresponding saturated body, which always exhibits a higher melting point. In the case of Olein, the commonest of the liquid oils, addition of less than 1 per cent. of Hydrogen effects the transformation to solid Stearin.

The lower unsaturated fatty acids are easily reduced. The same methods of reduction applied to Oleic acid, however, invariably give unsatisfactory or negative results (see Lewkowitsch, *J. Soc. Chem. Ind.*, 1897, 16, 389).

The reduction of Oleic acid to Stearic by means of red Phosphorus and Iodine, or Hydriodic acid, at a higher temperature was effected by Goldschmidt (*Sitz. b.d. Wiener Akad. d. Wiss.*, 72, 366), and adapted to a possible industrial process by de Wilde and Reychler, who heated Oleic acid to 280° C., with 1 per cent. of Iodine, in presence

of a tallow soap, and boiled the product with dilute acid, finally distilling the partially reduced oil and recovering the Iodine (*Bull. Soc. chim.*, 1889, (3), 1, 295; *Chem. Zeit.*, 1889, 13, 595). Chlorine and alkali in an autoclave at 120–150° C., in the theoretical proportions as calculated from the Iodine value of the oil, were proposed by Imbert, in place of Iodine (U.S.P. 901905 of 1908).

Chlorination of the fatty acid, and heating the chloro-acid with water in the presence of finely-divided Zinc or Iron was proposed by Zurrer (D.R.-P. 62407 of 1891). Tissier attempted a similar result by heating the fat in an autoclave with powdered Zinc and water (F.P. 263158 of 1897), whereby the fat was first hydrolysed and the free acid then reduced by the nascent Hydrogen generated by the action of the acid on the metal. Lewkowitsch, however, has stated that Zurrer's chlorination process in the case of Oleic acid gives back mainly the unsaturated acid, while Freundlich and Rosauer failed to confirm the method of Tissier (*Chem. Zeit.*, 1900, 24, 566).

Two methods have attained a limited application on the large scale. The scission of Oleic acid into Palmitic and Acetic acids is effected by heating with caustic Potash (Varentrapp's reaction: see *J. Soc. Chem. Ind.*, 1883, 2, 98; 1884, 3, 200), while heating with Zinc chloride at 185° C. brings about a considerable transformation to Hydroxy stearic acid. The same solid product has also been made by the action of Sulphuric acid on Oleic acid, followed by superheated steam.

✓ Electrolytic reduction was considered by Weineck and applied under various conditions by Magnier and Tissier (E.P. 3363 of 1900, D.R.-PP. 126446 and 132223 of 1899); Petersen (*Z. Elektrochem.*, 1905, 11, 549), Böhringer und Söhne (D.R.-PP. 187788 and 189332 of 1906), and by Waser (D.R.-P. 247454 of 1911). De Hemptinne obtained considerable reduction by exposing Oleic acid in thin films to the simultaneous action of an electric discharge and Hydrogen (U.S.P. 797112 of 1905).

Complete industrial success was not attained until the introduction of the catalytic method, suggested by the researches of Sabatier and Senderens, when enormous exploitation shortly followed, chiefly in connection with the manufacture of soap, candles, and edible fats (Margarine, etc.). The value of catalytic reduction was further increased by the fact that during the process the nauseating odour possessed by many oils of animal origin was completely destroyed, an odourless solid fat being produced. Hence an outlet was opened for fish and whale oils, which previously possessed no value apart from their Glycerine content.

Leprince and Siveke in Germany (D.R.-P. 141029 of 1902) and, almost simultaneously, Normann, in England (E.P. 1515 of 1903) discovered that the catalytic properties of Nickel were exerted

actively in liquid as well as in gaseous media, and that either liquid fat or its vapour, in presence of an active hydrogenating catalyst (Nickel, Cobalt, Iron, Copper, or a Platinum metal), was easily reduced by a current of Hydrogen.

The Normann patent was subsequently declared void in the British courts, since the specification was held not completely to describe the process, and in certain respects to be inaccurate. Thus, it failed to disclose that certain precautions were necessary in the preparation of the catalyst: that it must be reduced from the oxide, or other suitable compound, at a regulated temperature, that it must be free from certain anticatalytic substances, and preferably therefore not made from sulphate. The proportion of catalyst, and the working temperature, if maintained between certain limits, were stated to be immaterial, and only to affect the time required for hydrogenation. In actual fact, for each unsaturated substance there is an optimum temperature interval within which the reaction proceeds with the greatest facility, and a well-defined range outside which it cannot be effected at all. For most oils, the optimum point is between 175°C. and 200°C. , with a Nickel catalyst, and Hydrogen at atmospheric pressure, and the velocity of hydrogenation falls when the temperature departs from this range in either direction, but more rapidly when it is lowered than when it is raised. Rapid reduction in all cases is desirable, indeed essential in the manufacture of edible fats, both on account of the tendency of the catalyst to dissolve on prolonged contact with the oil, and also because of other changes setting in during long exposure to a high temperature which materially affect the quality (and taste) of the product.

The quantity of catalyst used likewise exercises an influence not explicable solely in terms of rate of reaction, a certain minimum proportion being in practice necessary in all cases. Thus, if Hydrogen is passed into linseed oil containing 0.5 per cent. of active Nickel in suspension, there may be practically no absorption even at 250°C. Using 1 per cent. of Nickel, absorption usually commences appreciably at 180°C. , increasing rapidly as the temperature is raised to 250°C. , while if 5 per cent. of Nickel is used, hydrogenation at 180°C. is much faster, and proceeds to a greater degree than when 1 per cent. of Nickel is used at 250°C. These results are probably due to the presence of small quantities of anticatalysts present in the oil, which paralyse small proportions of Nickel, so that the latter cannot operate unless an amount in excess of that inactivated by the poison is present.

Hydrogenation of oils is always carried out on the large scale in the liquid phase, and generally without a solvent. The usual hydrogenating catalysts are employed, namely, Palladium, Platinum, Nickel, Cobalt, Iron, and Copper, their activity for hydrogenation of

liquid oils following the order in which they are mentioned. All that has already been stated in regard to their preparation and conditions of activity holds also for hydrogenation of oils; but since hydrogenation of unsaturated substances is one of the easiest of catalytic reductions, a wider choice of means of preparation is available, good results still being obtained. The metals used in practice have been almost exclusively Nickel, Platinum and Palladium.

Nickel

Prepared by the methods of Sabatier, or of Brochet, or in any of the ways we have described, Nickel possesses powerful catalytic activity in the hydrogenation of unsaturated oils. According to Sabatier, exposure to atmospheric Oxygen gradually diminishes and ultimately destroys its activity, an observation referring in particular to gas phase reductions and which, for liquids, is an incomplete presentation of the facts. Presence of the following poisons must be excluded: Sulphur, Phosphorus, Arsenic, Halogens and their compounds, Ammonia, and oxides of Nitrogen.

The temperature at which Nickel oxide commences to be reduced, and consequently the catalytic activity of the resulting metal, varies according to the previous history of the oxide. Moreover, reduction of oxide to metal can never be carried to completion at the temperature at which reduction of Nickel oxide commences, no matter how prolonged the exposure of oxide to the Hydrogen. This anomalous behaviour has led to misconception as to the true nature of a nickel catalyst, and is the chief point of evidence in favour of the formation of a suboxide by the action of Hydrogen on oxide of Nickel.

Ipatiev showed that the hydrated oxide reduces much more easily than any form of oxide completely deprived of its combined water. Sabatier and Aboulenc confirmed this (*Bull. Soc. chim.*, 1912, 11, 641), and showed also that, whatever the form of the oxide, reduction to metal is never complete at temperatures below 300° C. Anhydrous Nickel oxide does not commence to reduce until about 300° C., reduces only slowly at 330° C., and not rapidly until 380° C. is reached. Even then, reduction is never complete, for which a temperature of 420° C. is necessary. Catalyst prepared from such oxide nevertheless hydrogenates the oxides of Carbon, Benzene, and Toluene, but is unsatisfactory with Phenols. Calcined Nickel oxide reduces with much greater difficulty, requiring a red heat for complete reduction, after which it fails to effect even the easiest reductions. Hydrated oxide, on the other hand, reduces and dehydrates slowly at 230° C., more rapidly at 270° C., rapidly at 300° C., and completely at 320° C.

The oxide formed when reduced Nickel oxidises rapidly by heating in air, or pyrophorically, is generally easier to reduce than the

oxide which originally supplied the pyrophoric metal. Thus, hydrated oxide of Nickel commences to reduce at 230°C . The metal obtained, when allowed to oxidise in air, yields an oxide which can be half reduced at 210°C . The anhydrous oxide reduces completely, as stated, at 420°C ., yielding a pyrophoric metal which, after rapid oxidation by heating in air, can be reduced at $280\text{--}320^{\circ}\text{C}$., furnishing an excellent catalyst. Exhausted catalysts can therefore be restored to full activity for oil hardening by atmospheric oxidation, followed by regulated reduction. Moreover, the catalytic activity of most metals or oxides, but especially in the cases of Nickel and Copper, varies with the reactivity of the metal or oxide for oxidation, or reduction, respectively.

The temperature of reduction of metallic oxides is often much lowered by the presence of a second oxide. Thus, the oxides of Nickel, Cobalt, and Copper are more easily reduced when two are present together in intimate admixture, the effect of Copper oxide being especially marked. Platinum, Palladium, and Silver compounds also lower the temperature of reduction of these oxides (Dewar and Liebmann, E.Ps. 12981 and 12982 of 1913; U.S.P. 1268692 of 1918; Ellis, U.S.P. 1156068 of 1915). The nitrate of one of the catalytic metals is dissolved in water with a smaller quantity of Copper nitrate, Silver nitrate, or Platinous chloride, and the mixture of oxides obtained either by precipitation or by evaporation and calcination. A mixture of Nickel and Copper oxides can be made in this way which is reduced in 2 hours at about 170°C . The use of such mixtures is especially advantageous when it is desired to reduce the oxide of the catalytic metal in presence of the substance to be hydrogenated, the lower temperature of reduction rendering this easily possible.

For reduction of Nickel oxide or hydroxide various temperatures, all below 300°C ., have been recommended by Sabatier and other investigators as follows: $245\text{--}250^{\circ}\text{C}$. (Darzens), $255\text{--}260^{\circ}\text{C}$. (Godchot), $270\text{--}280^{\circ}\text{C}$. (Brunel), and 280°C . (Leroux). These temperatures are considerably below the minimum at which any oxide of Nickel is completely reduced to metal, so that a catalyst still containing oxide must have been used by these investigators. Sabatier and Aboulenc showed that such incompletely reduced oxide was far more active catalytically than the completely reduced metal, the preparation of which required a higher temperature. In spite of this, Sabatier believed that the active agent was the free metal, a view he still maintained when Ipatiev, and, later, Bedford and Erdmann showed that Nickel, in the form of an oxide, behaved more energetically as a catalyst than when it was reduced in Hydrogen before use. The first action of the Hydrogen, Ipatiev supposed, consisted in reduction of some of the Nickel oxide, setting free the

metal in the nascent, and therefore superactive state. The work of Bedford and Erdmann, from which the conclusion was drawn that hydrogenation could be effected independently of the presence of free metal, is, briefly, as follows (*J. pr. Chem.*, 1913, 87, 425):—

Investigating the hydrogenation of oils, Bedford and Erdmann confirmed Ipatiev's results that the oxides of Nickel are more active than the free metal and less sensitive to anticatalytic impurities. For example, while Nickel is easily poisoned by traces of Sulphur, or halogens, Nickel oxide is much more resistant, and therefore more suitable for use with vegetable or animal oils, in which Sulphur compounds derived from proteid substances are liable to be present. Oxygen, Carbon monoxide, and other oxygen-containing gases are often strongly anticatalytic towards metallic Nickel, but exert merely a diluting action when present in the Hydrogen, if Nickel oxide is used. It is stated that Carbon monoxide may be allowed to accumulate up to 10 per cent. before renewing with pure Hydrogen. Either of the oxides of Nickel may be used, the sesquioxide, monoxide, or suboxide, but while the first two require a temperature of 250° C., 180–200° C. is sufficient for the last. At these temperatures the oxides can be used for hydrogenation of oils at atmospheric pressure, and induce a much faster rate of reaction than metallic Nickel. During the reaction, the higher oxides become partially reduced to the suboxide, and this appears to form a colloidal suspension in the oil, which assumes an inky-black appearance in consequence, while hydrogenation becomes faster owing to the more active form of the catalyst. Bedford and Erdmann claim that their experiments prove that no reduction to metallic Nickel takes place in the presence of oil, although in its absence reduction commences at 190° C. Thus, a used catalyst was separated and washed with Benzene, when a strongly magnetic black powder was obtained, intermediate in composition between NiO and metallic Nickel, and which Bedford and Erdmann therefore regarded as the suboxide. Like the metal, it dissolved in acids, giving Hydrogen, and in Nitric acid, giving oxides of Nitrogen, but it did not yield the carbonyl under conditions in which this substance is formed from metallic Nickel. Also, when compressed it formed a very feeble conductor of electricity as compared with the freshly-reduced metallic Nickel of Sabatier. ✓

In the expectation that the suboxide of Nickel believed to be formed during hydrogenation would be identical with the compound already prepared by Moore (*Chem. News*, 1895, 71, 82), Bedford and Erdmann reduced Potassium nickel cyanide electrolytically in the way described, and obtained an oxide of Nickel which possessed the same properties as a used Nickel oxide catalyst, being a black, magnetic powder which reduced Nitric acid, gave Hydrogen with the

other mineral acids, possessed the same very low electrical conductivity, and dispersed itself in a similar colloidal form in either oil or water. The oil suspension absorbed Hydrogen at a relatively low temperature, showing the substance to possess the same strong hydrogenating power.

The well-established fact that Nickel monoxide cannot be completely reduced at the temperature at which its reduction commences would seem to show that compounds intermediate between the monoxide and the metal exist. Sabatier and Espil, by observing the rate of reduction when Nickel oxide is exposed to the action of Hydrogen at varying temperatures, found that the rate of reduction up to about 72 per cent. of Nickel was much faster than subsequently. This break suggested the formation of an oxide, Ni_4O , which is less easily reduced by Hydrogen than the higher oxides (*C.R.*, 1914, 159, 668). Sabatier and Espil, however, obtained Nickel carbonyl easily from their reduction product, and from measurements of the rate of hydrogenation it induced inferred the existence of sufficient free metal to account for the results of Bedford and Erdmann.

The same conclusion was reached by Normann and Pungs, who pointed out that Bedford and Erdmann's experimental results fall far short of direct proof that Nickel suboxide is responsible for hydrogenation of oils (*Seifen. Z.*, 1915, 47, 191; *Chem. Z.*, 1915, several papers).

Normann and Pungs hydrogenated various oils with samples of pure and commercial Nickel oxide prepared in various ways as catalyst. The used Nickel oxide was then separated, and Bedford and Erdmann's tests were critically examined. The electrical conductivity of the washed powder was variable and always low, and the comparative results obtained with used catalyst, and with powders known to contain metallic Nickel, did not confirm Bedford and Erdmann's conclusions. An electro-magnet in the hydrogenating mixture attracted a portion of the catalyst of relatively high conductivity. Suboxide made by Moore's method was non-conducting, but after use as a hydrogenating catalyst its conductivity increased, indicating reduction to metal. The analytical determinations also indicated a higher content of Nickel than could be inferred from conductivity measurements and a higher proportion than would correspond with suboxide.

The dispersion to form an inky-black colloidal solution which a Nickel oxide catalyst undergoes during hydrogenation, said to resemble a property of Nickel suboxide, is no proof of the formation of this latter compound, since finely-divided metallic Nickel is black and decomposition of Nickel carbonyl in heated oil produces a very similar inky-black appearance.

The Nickel carbonyl test, it was shown, was carried out by Bedford and Erdmann in a very inconclusive manner. The carbonyl test is exceedingly sensitive to presence of air and certain other impurities, so that the Carbon monoxide used must be pure and dry. Simply pouring the hardened fat containing the catalyst from one vessel to another often sufficed to annul the test. Hence, after cooling the hardened fat and catalyst to 90–100° C., the Hydrogen was replaced by a current of Carbon monoxide. The gas leaving the reaction flask passed then through a hard glass tube heated at one point. In a number of experiments, using many different oils and preparations of catalyst, whereas a negative test was given before using, a marked Nickel mirror was obtained afterwards, often after a few minutes only of hydrogenation (*Chem. Zeit.*, 1915, 39, 29, 41). It was therefore concluded that hardening of fat did not occur in the absence of free metal, and that substances other than the free metal have not been proved to exert any catalytic influence.

The same critical examination of Bedford and Erdmann's data was applied by Meigen (*J. pr. Chem.*, 1915, 92, 390), by Meigen and Bartels (*J. pr. Chem.*, 1914, (2), 89, 290), and by Frerichs (*Arch. Pharm.*, 1915, 253, 512), who also concluded that there was no proof of suboxide formation and that Nickel oxides only yielded an active catalyst after some reduction to metal had taken place, which they therefore regarded as the active agent.

Bedford and Erdmann also showed that oxides of the other hydrogenating metals, notably Iron and Copper, are capable of inducing the hydrogenation of oils. They also found that a number of oxides powerfully promoted the action of Nickel oxide, such as small quantities of Alumina, Zirconia, Titania, Ceria, Lanthana, Magnesia, and Silver oxide. Promotion of hydrogenating catalysts is also the subject of a number of patents. Thus, the Badische Company promote the action of Nickel, Cobalt, Iron, or Copper by addition of "a high melting and difficultly reducible oxide," such as the oxides of the earth metals, rare earths, Beryllium, Magnesium, Manganese, Uranium, Vanadium, Niobium, Tantalum, Chromium, Boron, or Titanium, and also difficultly soluble oxy-acid salts, such as phosphates, molybdates, tungstates, and selenates of the earth metals, and of Lithium, or such reduction products of these salts as the selenites and chromites. The catalyst and promoter must be very intimately mixed, the two preferably being precipitated together from the same solution, or incorporated as fine precipitates while still in suspension. Impregnation of a promoting support (*e.g.*, Magnesia) with a Nickel salt is less satisfactory (E.P. 2306 of 1914). ✓

Spieler especially mentions gelatinous Aluminium hydroxide or Silicic acid as promoters (U.S.P. 1139592 of 1915). Bosch, Mittasch and Schneider have also found that complex fluorides (U.S.P.

1216933 of 1917) and the phosphates of the alkaline earths, especially Calcium phosphate (U.S.P. 1215335 of 1917), promote the action of hydrogenating catalysts when the two are precipitated in intimate contact.

Bedford and Erdmann obtained the basic patents for use of Nickel oxide catalysts, namely E.P. 29612 of 1910 (Bedford), D.R.-P. 62366 (Bedford, Erdmann, and Williams), and D.R.-P. 260009 (Bedford and Erdmann). An oxide in an especially voluminous and active form was obtained by mixing a strong solution of the nitrate of the metal with a water-soluble organic compound rich in Carbon (generally a carbohydrate, such as sugar or gum) and decomposing the mixture by allowing it to fall drop by drop upon a heated surface. The evolution of gas, brought about by oxidation of the Carbon and decomposition of the nitrate, produced a very light and active mass. (See also Schroeder, E.P. 10412 of 1901.)

Bedford and Erdmann also prepared catalysts from Nickel organic salts, such as the formate, in presence of the substance undergoing hydrogenation. They showed that Nickel salts as such do not act as catalysts, but in presence of the oil, heated to a suitable temperature, decompose either to oxide or metal in an active state. Nickel formate in presence of oil was stated to give the suboxide at 210° C., while at 250° C. free metal was formed. In the case of Nickel organic salts which do not so easily decompose, the catalyst was first formed by suspending the Nickel compound in oil and heating to a sufficient temperature—up to 260° C.—in a current of Hydrogen. The suboxide or metal then formed, and dispersed through the oil to form a black solution. When this was added to fresh oil, hydrogenation could be rapidly effected at 180–190° C. Thus, 3 grams of freshly-made Nickel oxide were added to 30 grams of cotton-seed oil, which was agitated and heated to 260° C. in a current of Hydrogen. A hardened oil, melting at 48° C., containing active catalyst in suspension was so obtained, which when added to 270 c.c. of fresh cotton-seed oil enabled the whole to be hydrogenated at 185° C. in 1 hour to a product melting at 45° C. (See also Fuchs, E.P. 11542 of 1913, and Bedford and Erdmann, U.S.P. 1200696 of 1916.)

Many other investigators have recommended the decomposition of an organic Nickel compound or salt. Soaps of the catalytic metal (Nickel, Iron, or Copper), preferably made from a fatty acid with a higher melting point than that of the saturated substance to be made, were proposed by de Kadt (E.P. 18310 of 1912). The advantage of the soaps is that they mix more intimately with the oil. Similar basic compounds of the higher fatty acids which dissolve in oil, and decompose at a high temperature in presence of Hydrogen, have been suggested by Hausmann (*Z. angew. Chem.*, 1914, 27, 63). Valpy and Lucas mentioned oxalates, tartrates, and

acetates of Nickel and Iron, and, in the case of Copper, the nitrate or carbonate, or organic salt such as the formate or oxalate which on heating evolve inert gases (E.P. 5847 of 1914). A powerful catalyst for reduction of oils or nitro-compounds is formed, which may be further improved by mounting upon an activating support, such as Magnesia or Alumina (D.R.-P. 282,568).

Wimmer and Higgins in a number of patents described the use of formates, acetates, lactates, fatty acid salts generally (including the soaps), and amido acid salts of the hydrogenating metals, especially Nickel (E.P. 18282 of 1912. F.Ps. 441097 of 1911, 454501 of 1913). Contrary to the accepted belief, these investigators held the view that a Nickel organic salt may as such exercise a catalytic action. The product of decomposition of a fatty acid salt of Nickel, Cobalt, Iron, or Copper in an inert liquid medium is, however, in an active state without the necessity of reduction and probably contains free metal (E.Ps. 29, 4144, 21041, 23873 of 1913; Dutch P. 2322 of 1918). According to Higgins, the presence independently of the catalyst of a volatile organic acid such as Formic accelerates hydrogenation (U.S.P. 1211704 of 1917), and the gaseous products of decomposition of the Formic acid may be employed to effect the hydrogenation (E.Ps. 23377 of 1912, 4665 of 1914).

By using a Nickel, or other metal salt, soluble in oil, and Hydrogen under high pressure, Richardson claimed the catalyst may be directly obtained in the oil in colloidal form (U.S.P. 1151718 of 1915). Kast obtained a voluminous oxide catalyst by decomposing the trinitrophenol salt of the catalytic metal (U.S.P. 1070138 of 1912).

Many methods of preparation of Nickel catalysts, varying only in detail from those we have already described, have been specified in the patent and other literature, these having reference especially to treatment of the Nickel compound used, the use of a support and the mode of impregnation, and the use of promoters. On the whole, commercial Nickel carbonate (basic, and hydrated, and free from catalytic poisons) appears to have been the most usual source of Nickel catalysts, this being reduced by passage along a sloping rotating cylinder, kept at a regulated temperature, through which a current of Hydrogen is passing in the reverse direction. Conditions of reduction leading to maximum formation of "suboxides," such as long treatment at a low temperature, or brief treatment at a higher, produce the most active catalyst (Boberg, E.P. 4702 of 1912, U.S.P. 1093377 of 1914; Burchenal, U.S.P. 1226945 of 1917). A promoting siliceous support further increases the activity of catalysts prepared in this way. Nickel hydroxide, precipitated from a Nickel solution by the addition of the theoretical quantity of Ammonia, has been preferred by Wesson (U.S.P. 1143339 of 1915) and by Woodruff (U.S.P. 1143343 of 1915).

Simple ignition at a suitable temperature of the formate of Nickel, Cobalt, Iron, or Copper in an inert atmosphere gives an active metal, the method being especially suitable for coating a support (Snelling, U.S.P. 1122811 of 1914). Silicates, borates, titanates, chromates, and uranates, prepared by precipitation with a Nickel salt, have been much advocated as hydrogenating catalysts, the presence of the acidic radical promoting the action of the metal (Byrom, E.P. 13382 of 1913, F.P. 470364 of 1914; Schoenfeld, *Seifen. Z.*, 1914, 945; Sulzberger, U.S.Ps. 1143332 and 1156068 of 1915; Erdmann and Rack, *Seifen. Z.*, 1915, 3, 46; Bosshard and Fischli, *Z. angew. Chem.*, 1915, 28, 365; E.P. 4023 of 1915; U.S.Ps. 1182995, 1199032, 1201226 of 1916; Swedish P. 41331 of 1916; E.P. 8130 of 1916; *Z. angew. Chem.*, 1916, 29, 39; Canadian P. 181287 of 1917; Ellis, U.S.Ps. 1266782 and 1255590 of 1918).

✓ Nickel hypophosphite when boiled precipitates metallic Nickel, which is catalytically active if the deposit is obtained in a fine powdery form rather than in coarse granules. Nickel sulphate (20 grams) is dissolved in water (100 c.c.), heated to 100° C., and Sodium hypophosphite (70 grams) added slowly with agitation. The reduction is complete in 1 hour, when the Nickel is washed free from sulphate. Palladium can be made similarly, and is very effective (Breteau, *Bull. Soc. chim.*, 1911, 9, 515).

Hydrazine as reducing agent has been recommended by Sulzberger (Canadian P. 181447 of 1918). The powerful reducing action that this substance exerts on metallic salts is increased by the presence of a metal of the Platinum group, which may be present in colloidal solution. A Nickel salt so treated gives a black, non-pyrophoric powder, containing Nickel and the Platinum metal in intimate admixture.

The advantages of catalytic Nickel in a flaky form have been described by Hagemann and Baskerville (U.S.P. 1083930 of 1914), and the preparation of a finely-divided Nickel based upon Bredig's colloidal Platinum method has been patented by Ellis (U.S.P. 1092206 of 1914) and by Richardson (U.S.P. 1151045 of 1915). An electric arc formed between Nickel poles beneath the surface of a liquid throws off particles of metal of different sizes, of which the more finely-divided can be separated by levigation.

Colloidal Nickel can be obtained by passing Hydrogen through a solution of Nickel formate and Gelatine in Glycerine at 200–210° C. (Kelber, *J. Ind. Eng. Chem.*, 1918, 396).

Nickel carbonyl also is a satisfactory source of active catalytic Nickel. Mond, Langer, and Quincke noticed that when Carbon monoxide was passed over finely-divided Nickel at a temperature below 100° C. a volatile compound of Nickel, Ni(CO)_4 , was produced. A complete description of the Mond Nickel plant subsequently

erected at Clydach, South Wales, is given by Coleman, "The Nickel Industry," Canadian Department of Mines publication 1913.

Nickel carbonyl boils at 43°C . (751 mm.), is soluble in the usual organic solvents, is inert to dilute acids and alkalis, but is oxidised by air or dilute Nitric acid, and is dissociated into Nickel and Carbon monoxide on heating, the dissociation pressure exceeding 1 atmosphere at $120\text{--}130^{\circ}\text{C}$. and rapidly rising with the temperature. Subjected to shocks, a more or less violent explosive decomposition may occur.

Nickel carbonyl dissolves in oils, and when dissociated by heating the oil solution, the Nickel separates in a very finely-divided form, imparting an inky-black appearance to the oil, and remaining in suspension even on standing for several weeks. In this form its catalytic activity is very great. For example, cotton-seed oil, containing 0.5 per cent. of its weight of Nickel, formed from the carbonyl, was treated with Hydrogen at the ordinary pressure for about 1 hour, when a solid product melting at 47.6°C . was obtained (Ellis, "Hydrogenation of Oils," London, 1919). The main difficulty in the application of the Nickel carbonyl method is in the separation of the finely-divided catalyst from the hardened oil. The separated powder is still powerfully active, and retains its activity for a long time with oils reasonably free from anticatalysts.

Modifications of the method consist in mixing a suitable proportion of Nickel carbonyl vapour with the Hydrogen and passing it into the oil heated to the reaction temperature, when the Nickel is formed in a finely-divided state in intimate contact with the Hydrogen and effects rapid reduction. Alternatively, the heated oil may be atomised with Hydrogen, the Nickel carbonyl being contained either in the oil or the gas, or the oil containing the carbonyl may be caused to flow at 180°C . down towers fitted with baffles, and containing Hydrogen (U.S.Ps. 1095144 of 1914, 1138201 and 1154495 of 1915, 1251202 of 1917). Either of these methods gives a very rapid reaction.

By the method of liquefaction, which possesses the advantage of removing catalytic poisons, Lessing made from water gas a mixture of Hydrogen with a low percentage of Carbon monoxide. When this gas was passed over warm, finely-divided Nickel, sufficient of the metal was picked up as carbonyl to effect very rapid hydrogenation of an oil into which the gas stream then passed. This procedure was particularly effective, the catalyst probably acting at the moment of its formation, and the continuous small supply enabled complete hydrogenation to be obtained using a total amount of Nickel not greater than 0.1 per cent. of the amount of oil. The same amount of Nickel carbonyl added at once to the oil effected comparatively insignificant results (E.P. 18998 of 1912).

Lessing has also patented an ingenious hydrogenation apparatus

in which the catalyst as carbonyl, the oil (preheated), and the Hydrogen are brought together by spraying through a nozzle under pressure (U.S.P. 1162623 of 1915).

In an investigation on the hydrogenating activity of base metal catalysts at ordinary temperatures and pressures, Kelber showed that, weight for weight, the power of Nickel or Cobalt is enormously increased by mounting upon certain supports (*Ber.*, 1916, 49, 55). Thus, Nickel obtained by reduction with Hydrogen at 450° C. is hardly active at the ordinary temperature, but if the carbonate or other Nickel compound is spread over a suitable support, and reduced at 450° C., the product is superior to catalysts prepared at low temperatures in the absence of a support. The supports mentioned were bodies containing well-marked promoting substances, such as infusorial earths, or kieselguhr, finely-divided hydrated silicates of Magnesium and Aluminium, and various forms of charcoal. The results were established by the hydrogenation of a number of substances at the ordinary temperature, viz., Cinnamic acid, Sodium cinnamate, Sodium propionate, $C_6H_5 \cdot C \equiv C \cdot COONa$, Quinine hydrochloride, Diphenyl diacetylene, $C_6H_5 \cdot C \equiv C \cdot C \equiv C \cdot C_6H_5$, and the Sodium soap from cotton-seed oil. The hydrogenation was fastest in aqueous-alcoholic solution, slower in Alcohol, Acetone, Ether, or Ethyl acetate, but markedly accelerated by addition of a little water. Acetic acid also was a satisfactory solvent, while Chloroform was not. Cobalt was active, but much slower than Nickel.

Supports for a Nickel catalyst most commonly mentioned in the patent literature are :—

1. Infusorial earth, kieselguhr, or fuller's earth (Crossfield, E.P. 30282 of 1910; Kaiser, U.S.P. 1004034 of 1911; Morey and Craine, U.S.P. 1232830 of 1917; Bacon and Nicolet, U.S.P. 1152591 of 1915; Schicht, Austrian P. 70771).

2. Various forms of charcoal, which both support the catalyst and occlude the Hydrogen (Ellis, U.S.P. 1060673 of 1913, 1156674 of 1915; Ittner, U.S.P. 1238774 of 1917).

3. "Complex insoluble compounds, containing one or more easily replaceable bases," e.g., a complex silicate like permutite (E.Ps. 1358 and 8452 of 1915; U.S.P. 1256032 of 1918).

4. Nickel sheet or wire or other metal, carrying a coherent layer of Nickel oxide (Hagemann and Baskerville, U.S.P. 1238137 of 1917, Elworthy, U.S.P. 943627 of 1909).

Poisons. While the "caprices" of catalytic reactions and the different results claimed by different investigators of such reactions are in large measure due to the influence of anticatalysts, more extensive experience has shown that if the catalyst, in its composition and mode of preparation, is adapted for the reaction it is required to induce, the effect of anticatalysts is far less considerable

than at first appeared. Thus, in his earlier experiments, Sabatier was unable to hydrogenate pure Phenol which had been exposed overnight to an atmosphere containing Bromine fumes. Sabatier and Espil (*Bull. Soc. chim.*, 1914, 15, 778), returning to the subject of catalytic poisoning, found that Benzene containing 0.5 per cent. of Iodine in solution was converted into Cyclohexane, only the catalyst in the fore part of the catalytic tube being affected. Chlorine and Bromine introduced as the acids, or as Chlorobenzene, also Sulphur in the form of Carbon disulphide, similarly inhibited the action of part only of the catalyst, this extracting the poison and enabling the remainder to function. Nickel which had been rendered inert for hydrogenation of Benzene retained its power to reduce nitriles, but failed with aldehydes, ketones, and ethylenic hydrocarbons, and while Chlorine-poisoned Nickel could be almost completely revived by using for reduction of Nitrobenzene, poisoning by Bromine or Iodine could not be cured in this way.

That poisons exert their action by combining in some way with the catalyst is definitely established, and this property has been employed in various ways for removing anticatalytic impurities from reacting substances. For example, Schroeter purified Naphthalene by heating with finely-divided metals, and in gas reactions, such as the synthesis of Ammonia, a "protector furnace" filled with exhausted catalyst is commonly employed. For the purification of low-grade oils, the oil may be agitated at 180–200° C. with a suitable amount of stale catalyst, filtered, and hydrogenated with fresh catalyst (U.S.P. 1132710 of 1915). Ellis and Wells have carefully studied the effect of different poisons in various concentrations, and have shown that low grade oils can best be hydrogenated by gradual addition of fresh catalyst (*J. Ind. Eng. Chem.*, 1916, 886).

Sulphates have often been assumed to exert a deleterious influence, but Ellis has shown that when hydrogenation is carried out at temperatures at which sulphates are stable, or when only difficultly reducible sulphates (e.g., Sodium sulphate) are present, no anticatalytic effect is produced at temperatures below 250° C. Sulphuretted hydrogen or sulphides are much more serious poisons

Kelber has examined quantitatively the sensitiveness of catalytic Nickel prepared in different ways towards Hydrocyanic acid and cyanides, Sulphuretted hydrogen and Carbon disulphide (*Ber.*, 1916, 49, 1868). When prepared from basic Nickel carbonate by reduction in Hydrogen, the Nickel showed a diminishing sensitiveness in the following order: that reduced at 450° C. was most sensitive; reduced at 310° C. the sensitivity was less; mounted on certain inorganic carriers that have been already mentioned and reduced at 450° C. its sensitiveness was enormously diminished.

Richter and van Arsdel compared the rates of hydrogenation

when pure Nickel was used with the corresponding rates in presence of various foreign substances. Oil containing 1 per cent. of pure Nickel catalyst was first hydrogenated for 1 hour, and the rate of hydrogenation determined by measurement of Iodine values. The foreign body was then added and hydrogenation continued. Sulphuretted hydrogen, Sulphur dioxide, Chlorine, and Sulphur (in quantities of 2 per cent. of the Nickel) immediately destroyed all activity. Sodium sulphide gradually rendered the catalyst inert. Sodium chloride, sulphate, or nitrate, Nickel chloride, and reduced Iron had no effect.

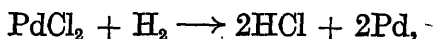
Carbon monoxide is a marked inhibitant except in the case of Nickel prepared from the carbonyl, for which difference no explanation can be offered. Catalyst which has become fatigued by use in the hydrogenation of oils can be regenerated by pressing out the oil, burning the residual organic matter, and reducing to the metal in Hydrogen at a regulated temperature (Sabatier and Aboulenc, *Bull. Soc. chim.*, 1912, 11, 641; Morrison, U.S.P. 1203233 of 1916). Adhering fat can first be removed by saponification with water under pressure (Haas, Norwegian P. 28034 of 1917).

✓ Platinum and Palladium

The Platinum metals have received considerable attention in connection with the hydrogenation of oils, since their high initial cost is largely offset by their extraordinary efficiency. Very small quantities suffice, and considerable advantages accrue from the use of a low temperature.

Fokin first employed Platinum and Palladium for hydrogenation of oils, and he regarded the latter as the most active catalyst known for this purpose. Using Palladium-black, linseed, castor and cod-liver oils were completely reduced at temperatures much below 100° C. Platinum-black under the same conditions was less effective.

Paal employed these metals in colloidal solution, and hydrogenated completely castor, olive, sesame, fish oils and animal fats. Later, he found that the preformed colloidal solution was not necessary, that the chlorides, or other salts of Platinum or Palladium, with a neutralising agent such as sodium carbonate, could be directly added to the oil, and Hydrogen passed at a suitable temperature (U.S.P. 1023753 of 1912). The powdered salts are intimately mixed by trituration, or a similar method, with the substance to be hydrogenated, and Hydrogen, preferably under several atmospheres pressure, allowed to act upon the mixture, which is vigorously stirred at a convenient temperature, not above 100° C. The Platinum or Palladium compound is first decomposed into the free metal,



which becomes distributed in a finely-divided form throughout the oil, and exerts a much more powerful action than the same weight of metal in the form of "black." Very small quantities of the catalyst suffice; thus, 1.7 parts of Palladium chloride (= 1 part of Palladium) in the presence of Hydrogen converts 10,000 parts of fat, or fatty acid, into solid masses within 3 or 4 hours, whereas the oil is still liquid after 12 hours if the same weight of Palladium-black is used. Paal gives the following example: 1,000,000 parts of castor oil or Oleic acid are thoroughly mixed with suitable quantities of a well-powdered, anhydrous salt of Platinum or Palladium, such as 34 parts of PdCl_2 (= 20 parts of Pd), 140 parts of PtCl_2 (= 100 parts of Pt), 172 parts of PtCl_4 , or 230 parts of H_2PtCl_6 , in each case with, or without, an equivalent of Sodium carbonate. The mixture is placed in a pressure vessel, fitted with an agitator and pressure gauge, and Hydrogen admitted to 2 to 3 atmospheres. The mixture is then heated with stirring, to about 80°C ., and the progress of hydrogenation followed by the fall of pressure, fresh quantities of gas being added as it is consumed. The hydrogenation is complete when the pressure remains steady for a considerable time, and the product is then discharged to a heated filter-press, where the catalyst is collected and almost completely recovered.

The catalyst can be employed almost indefinitely if poisons, of which Lead is one of the most serious, are excluded. Carriers without anticatalytic action, such as carbonates of Copper or Magnesium, can with advantage be used, and make the process of catalyst recovery easier. Since acids may exert an inhibiting influence and are formed when the salt of the catalysing metal is decomposed, it is usually desirable to add an equivalent of a neutralising agent, such as Sodium carbonate.

Skita's method, also, has been adapted to the hydrogenation of oils (Skita and Boehringer und Söhne, U.S.P. 1063746 of 1913). In the presence of an oil, the addition of a protective colloid is unnecessary, the oil serving the same function. The unsaturated substance is suspended or dissolved in a suitable medium, a small amount of a Palladium or Platinum salt added, and the whole exposed to the action of Hydrogen, preferably under a slight pressure. The addition of an acid, such as Hydrochloric, is stated under these circumstances to be an advantage, but with fats is unnecessary. For example, 50 grams of olive oil are suspended in a solution containing 0.05 gram of Platinous chloride, 20 c.c. of alcohol, 50 c.c. of water, and 8 c.c. of dilute Hydrochloric acid. When treated with Hydrogen at 4 atmospheres pressure, and 70°C ., a solid fat is quickly formed. Castor oil (250 grams) is similarly hydrogenated when mixed with a solution of about 0.05 gram of Palladium chloride in 5 c.c. of water, and stirred in an autoclave at 70°C . with Hydrogen at 4 atmospheres

pressure (F.P. 447420 of 1912, E.Ps. 18996, 28754 of 1912, and 16283 of 1913). The colloidal hydroxides of Palladium or Platinum, as prepared by Skita's method, can also be used (Meyer, *Diss.*, Karlsruhe, 1912). Albright used these colloidal metals to measure the unsaturation values (Hydrogen numbers) of essential oils (*J. Am. C.S.*, 1914, 2188).

The poisoning effect of metals and their compounds, especially Lead, on Platinum and Palladium catalysts (Paal and Karl, *Ber.*, 1913, 46, 3069; Paal and Windisch, *ibid.*, 1913, 46, 4010) has already been described. According to Skita, hydrogenation is sometimes retarded by presence of acids (*Seifen. Z.*, 1914, 1213).

According to Mannich (*Seifen. Z.*, 1914, 1174) and Mannich and Thiele (*Ber. Deut. Pharm. Ges.*, 1916, 26, 36) a Platinum catalyst mounted on charcoal (e.g., purified animal charcoal) is more efficient than any other form. Powdered ignited animal charcoal is shaken with Hydrogen and a 2 per cent. solution of Palladium or Platinum chloride until no more gas is absorbed. The powder is then washed and dried, and remains unaltered in air. This catalyst can be used with various solvents and is easily separated by filtration without leaving any trace of metal in the hydrogenated product. Since Platinum or Palladium and charcoal absorb large volumes of Hydrogen, such a mixture is exceedingly rapid in action as a hydrogenating catalyst.

The use of Platinum or Palladium mounted on a suitable support has also been advocated by Verona-Rinati (*Ann. Chim. Appl.*, 1914, 99), and Ellis (U.S.P. 1174245 of 1916).

Lehmann has effected the hydrogenation of unsaturated fatty acids by the use of Osmium tetroxide, which in presence of Hydrogen is reduced to a colloidal solution of Osmium tetrahydroxide. From 10 grams of olive oil, with 0.05 gram of Osmic acid, a fat melting at 39° C. was produced in 1½ hours by passing Hydrogen at ordinary pressure (*Arch. Pharm.*, 1913, 153; *Seifen. Z.*, 1913, 418). Normann and Schick, however, hold that reduction to metallic Osmium occurs, and that this is responsible for the hardening (*Seifen. Z.*, 1914, 1111). Ruthenium and other Platinum metals also have been favoured as catalysts for hydrogenation of oils (Mittasch, U.S.P. 1173532 of 1916).

Various patents advocate supplying the Hydrogen for hydrogenation of oils in the form of Formic acid. In presence of Platinum or Palladium-black, this is decomposed, and the Carbon monoxide liberated, while the Hydrogen enters into combination with the oil (Thron, U.S.P. 1077442 of 1913).

The recovery of Platinum or Palladium from the hardened oil is one of the most important technical difficulties attending their use. The completeness of the recovery naturally depends upon

various factors. When the metal is finely divided, or colloidal, addition of a flocculating agent (such as a strong electrolyte) may be necessary before the metal can be filtered off. When Palladium is used under such conditions, a loss amounting to 5 to 7 per cent. of that used may occur (Connstein). According to Bergius, the loss is about 1 gram of metal per barrel of fat hydrogenated (Fahrion, "Die Hartung der Fette," 1915). Such losses are minimised by mounting the catalyst upon an easily filterable support; preferably carbonaceous, which by virtue of its absorptive properties assists the reaction and renders recovery of Platinum or Palladium from spent catalyst a comparatively simple matter; the metal remaining after burning away the impurities in air.

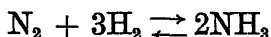
CHAPTER IX

AMMONIA

Historical. Theoretical. Preparation of the Gases, and their Purification. Catalysts. Separation of Ammonia: (a) Liquefaction, (b) Water Solution. The Haber Process, and the British, American, Italian, and Norwegian Modifications. The Claude Process.

“ALKALINE air” was isolated in 1774 by Priestley, the discoverer of Oxygen, who also found that when electric sparks were passed through it, a large increase of volume occurred, and the residual gas was inflammable. Berthollet, in 1785, identified Hydrogen as a product of this action, while Austin (1788), Davy (1800), and Henry (1809) established that the passage of electric sparks resolved 2 volumes of Ammonia into 1 volume of Nitrogen and 3 volumes of Hydrogen.

The reversibility of the action



was inferred from the researches of Deville (*C.R.*, 1865, 60, 317; “Leçons,” p. 64), who showed that the decomposition of Ammonia into Nitrogen and Hydrogen by electric sparks was never complete, and Donkin (*Proc. R.S.*, 1873, 21, 281), who caused Nitrogen and Hydrogen to combine completely by prolonged sparking, when these gases were confined in a eudiometer tube over dilute acid.

The formation of Ammonia in small quantities when a mixture of Nitrogen and Hydrogen was passed over a heated catalytic substance (*e.g.*, finely-divided Iron or Manganese) had been noticed by several experimenters, and application of Le Chatelier’s Law had suggested the use of pressure to increase the amount of combination. Thus, as far back as 1884, Ramsay and Young passed a mixture of Nitrogen and Hydrogen over a heated Iron wire, and established the presence of Ammonia in the resulting mixture.

Ilavati proposed to synthesise Ammonia by passing a mixture of Nitrogen and Hydrogen through a heated vessel containing a mixture of Titanium, or a titaniferous body, with Platinum, mounted upon a porous support (Austrian P. 45/2938 of 1895). A Norwegian company, the Christiania Minekompanie, in French P. 225183 of 1896, claimed the formation of Ammonia when a mixture of Nitrogen

and Hydrogen was passed over heated Titanium, precipitated in a finely-divided state on a neutral support, with or without the addition of Platinum or a Platinum metal. They further claimed that Titanium could be replaced by Antimony, Bismuth, or an alkali or alkaline-earth metal associated in each case with smaller quantities of a Platinum metal.

The formation of Ammonia by the alternate passage of Nitrogen and Hydrogen over heated spongy Iron had been demonstrated by Dufresne, who, under the name of "Charles Tellier," obtained a number of patents. Thus, according to E.P. 1833 of 1865, which dealt with the preparation of Oxygen from air, the large quantities of Nitrogen obtained as a bye-product were to be utilised by absorption in red-hot spongy Iron, and passing Hydrogen over the combination, when considerable quantities of Ammonia were produced. D.R.-P. 17070, and F.P. 138472, both of 1881, then proposed to effect the union of Nitrogen and Hydrogen by passing the gases alternately over red-hot spongy Iron, the gases being made by the action of air, or steam, respectively, on Zinc. In the former patent, D.R.-P. 17070, the Société Azote de Paris and "Charles Tellier" covered all the stages of their proposed process, viz., the preparation of the gases, their passage alternately over a suitable heated catalyst, consisting of spongy titaniferous iron, alone, or mixed with another metal, or Platinum deposited upon pumice or charcoal. The use of pressure "up to 10 atmospheres" was also declared an advantage.

Du Motay devised a continuous process for the production of Ammonia by alternate passage of Nitrogen and Hydrogen over red-hot Titanium nitride (F.Ps. 92346 of 1871 and 138472 of 1881). The higher nitrides of Titanium, Ti_3N_2 and TiN , react with Hydrogen to give Ammonia and a lower nitride, probably Ti_2N_3 , which is reconverted by Nitrogen into one of the higher.

The Haber process was anticipated by Le Chatelier in 1901 (F.P. 313950), who caused Nitrogen and Hydrogen to combine at high pressure in contact with a catalyst. Unfortunately, a serious explosion wrecked his apparatus, and deterred Le Chatelier from undertaking further high pressure experiments. Perman, however, confirmed all his results (*Proc. R.S.*, 1905, A, 76, 167) and mentioned the following metals as catalysts: reduced finely-divided Iron, Cobalt, Nickel, Palladium, and Copper.

The technical development of the high pressure Ammonia synthesis originated in the work of Haber and his co-workers, especially van Oordt, Le Rossignol, and, later, H. C. Greenwood. Commencing in 1904, the equilibria between Nitrogen, Hydrogen, and Ammonia were exhaustively studied in presence of different catalysts and at temperatures and pressures varying over wide ranges (*Z. anorg. Chem.*, 1905, 43, 111; 44, 341; 47, 42; *Ber.*, 1907, 40, 2144; *Z.*

Elektrochem., 1908, 14, 181, 513). These investigators showed conclusively that, with certain precautions and perfection of apparatus, Ammonia could be synthesised continuously at high pressure, industrial success depending upon this continuous action, and in 1910 Haber commenced the technical exploitation of his results on behalf of the Badische Anilin- und Soda-Fabrik. Owing largely to the achievements of Dr. C. Bosch, who developed and organised the manufacture and purification of the enormous volumes of gases required, and in spite of many other difficulties, this company brought the process to a brilliant technical success, independently, in the later stage, of the original discoverer. Their first large-scale plant erected at Oppau, on the Rhine, commenced manufacturing in 1913, and steadily increased in importance, as the following figures for its production show:—

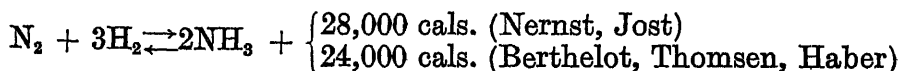
| Year. | Approximate production of (NH ₄) ₂ SO ₄ (tons). |
|----------------|--|
| 1913 | 20,000 |
| 1914 | 60,000 |
| 1915 | 150,000 |
| 1916 | 300,000 |
| 1917 | 500,000 |

About 1919, the Badische Company erected much larger plant at Merseburg, in Saxony, and the combined annual production of the two factories has reached the astounding amount of 500,000 tons of anhydrous Ammonia.

Simultaneously with the great technical developments in Germany, all the nations allied during the war, and several others, fostered research, and encouraged the erection of experimental plants. In most cases, development followed closely the lines of the Badische-Haber-Bosch method, although no details of this process were divulged except in patent specifications which were calculated to mislead. In France only was any considerable new departure made, where Claude, in collaboration with the "Société L'Air Liquide," perfected apparatus for the use of "super-pressures," and evolved a process in certain respects more advantageous than the original Haber. Our description of the Haber-Bosch process will therefore include its numerous variations, the "Casale," "Cederburg," "Fauser," etc., while we shall devote a separate section to consideration of the Claude process.

Theoretical

From the equation



it is apparent that increasing pressure favours the combination of Nitrogen and Hydrogen, while increasing temperature favours the dissociation of Ammonia.

Haber first investigated the equilibrium between Nitrogen, Hydrogen, and Ammonia at the ordinary pressure, at temperatures between 700° C. and 1000° C., using Iron, Chromium, Nickel, and Manganese as catalysts, to assist in the attainment of equilibrium. As a result of experiments in which both the union of Nitrogen and Hydrogen, and the dissociation of Ammonia were studied, Haber obtained the following values for the percentage of Ammonia present in the equilibrium mixtures :

| Temperature (°C.). | Ammonia (per cent.). |
|--------------------|----------------------|
| 700 | 0.0221 |
| 800 | 0.0109 |
| 850 | 0.0091 |
| 1000 | 0.0048 |

(*Z. anorg. Chem.*, 1905, 43, 111; 44, 341; 47, 42; *Ber.*, 1907, 40, 2144; *Z. Elektrochem.*, 1908, 14, 181, 513).

This equilibrium was studied independently by Jost, at pressures up to 70 atmospheres (*Z. Elektrochem.*, 1907, 13, 521; 1908, 14, 373) and theoretically, in the basis of his recently developed heat theorem, by Nernst (*Z. Elektrochem.*, 1910, 16, 96). The experimental and theoretical results of these investigators were in remarkable agreement, but somewhat at variance with the equilibrium proportions, and thermal values of the reaction, as determined by Haber—whose figures were subsequently modified accordingly. Latterly, the equilibrium has been investigated with great care by many investigators, at pressures to 200 atmospheres and temperatures to 1000° C. Claude (*C.R.*, 1919, 169, 1039) determined the equilibrium composition at pressures to 1000 atmospheres, but his results were probably low, since the conditions of experiment were such that equilibrium may not have been established. He showed, however, that the velocity constant of the reaction does not alter, and that the van 't Hoff relations hold at pressures up to 1000 atmospheres.

The most recent and complete investigations are by Larson and Dodge (*J. Am. C.S.*, 1923, 45, 2918) and by Larson (*ibid.*, 1924, 46, 367), who determined experimentally the percentage of Ammonia present in equilibrium mixtures made from 1 volume of Nitrogen and 3 volumes of Hydrogen at pressures of 10, 30, 50, 100, 300, 600, and 1000 atmospheres and temperatures ranging from 350° C. to 500° C., and completed the series tabulated by theoretical computa-

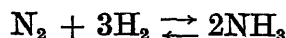
tion. For completeness, other available figures also have been added.

| Temp. °C. | Percentage of Ammonia in Equilibrium Mixtures, at the Pressures (in atmosphere) indicated. | | | | | | | |
|--------------|--|-------|-------|-------|-------|-------|-------|-------|
| | 1 | 10 | 30 | 50 | 100 | 300 | 600 | 1000 |
| 200 | — | 50.66 | 67.56 | 74.38 | 81.54 | 89.94 | 95.37 | 98.29 |
| 250 | — | 28.34 | 47.22 | 56.33 | 67.24 | 81.38 | 90.66 | 96.17 |
| 300 | — | 14.73 | 30.25 | 39.41 | 52.04 | 70.96 | 84.21 | 92.55 |
| 350 | — | 7.41 | 17.78 | 25.23 | 37.35 | 59.12 | 75.62 | 87.46 |
| 400 | — | 3.85 | 10.15 | 15.27 | 25.12 | 47.00 | 65.20 | 79.82 |
| 450 | 0.0213 | 2.11 | 5.86 | 9.15 | 16.43 | 35.82 | 53.71 | 69.69 |
| 500 | 0.0122 | 1.21 | 3.49 | 5.56 | 10.61 | 26.44 | 42.15 | 57.47 |
| 550 | 0.0769 | 0.76 | 2.18 | 3.45 | 6.82 | 19.13 | 31.63 | 41.16 |
| 600 | 0.0489 | 0.49 | 1.39 | 2.25 | 4.52 | 13.77 | 23.10 | 31.43 |
| 650 | 0.0321 | 0.33 | 0.96 | 1.53 | 3.11 | 9.92 | 16.02 | 20.70 |
| 700 | 0.0229 | 0.23 | 0.68 | 1.05 | 2.18 | 7.28 | 12.60 | 12.87 |
| 750 | 0.0159 | — | 0.47 | — | 1.50 | 4.50 | — | — |
| 850 | 0.0089 | — | 0.26 | — | 0.87 | 2.60 | — | — |
| 950 | 0.0055 | — | 0.16 | — | 0.54 | 1.50 | — | — |

Since the equilibrium percentage of Ammonia sinks so rapidly with rising temperature, it is surprising that, as shown by Deville, Donkin, and later by Perman, a measurable proportion should be formed at atmospheric pressure from Nitrogen and Hydrogen at the temperature of the electric arc. This matter has been examined theoretically and experimentally by Maxted (*J. Soc. Chem. Ind.*, 1918, 37, 105T, 232T; *J.C.S.*, 1918, 113, 168, 386; 1919, 115, 113; E.P. 130023 of 1917). This investigator pointed out that, from the equation

$$\text{Log } K = \frac{2215}{T} - 3.625 \log T + 0.000307 T + 0.29 \times 10^{-6} T^2 + 4.82,$$

it would appear that the equilibrium constant of the reaction



should first fall with the temperature, attain a minimum, and then again rise, as follows:—

| T. (degrees Absolute). | K × 10 ⁴ . | | | | |
|------------------------|-----------------------|---|---|---|-------|
| 1000 | . | . | . | . | 5.7 |
| 2000 | . | . | . | . | 0.78 |
| 3000 | . | . | . | . | 3.03 |
| 4000 | . | . | . | . | 152.0 |

The equation is based upon thermal constants accepted by Haber, the accuracy of which has been questioned. Maxted has shown,

however, that whichever thermal constants are accepted, though the corresponding values of K differ, they nevertheless still tend to a minimum, and then rise, the points of minimum value differing widely in the several cases.

The high temperature equilibria were investigated experimentally by (a) injecting Nitrogen and Hydrogen into flames, and rapidly cooling the products of combustion, (b) rapidly cooling mixtures of Nitrogen and Hydrogen that had passed a high tension arc. In the one case, Nitrogen was added to an oxy-hydrogen flame burning under the surface of water. Formation of Ammonia was demonstrated. Equilibria at the temperature of the arc were investigated both by synthesising Ammonia and by decomposing it, so approaching the equilibrium from both sides. The most effective arc was made by bringing the secondary terminals of an induction coil close together, until the spark discharge was apparently a continuous high tension arc of high temperature. A spark discharge had a comparatively feeble effect.

By comparing the time of contact with the arc and the percentage of Ammonia in the resulting gaseous mixture, the following results were obtained:—

| Synthesis of Ammonia. | | Decomposition of Ammonia. | |
|---|------------------------|---|------------------------|
| $10^4 \times$ time of contact in seconds. | Ammonia by volume (%). | $10^4 \times$ time of contact in seconds. | Ammonia by volume (%). |
| 0 | 0 | 0 | 3.0 |
| 6 | 0.7 | 7 | 2.5 |
| 15 | 1.1 | 17 | 2.2 |
| 32 | 1.4 | 30 | 2.0 |
| 41 | 1.5 | 42 | 1.8 |

These results indicate an equilibrium mixture at the temperature of the arc containing 1 to 2 per cent. of Ammonia. Maxted also found that an increase of pressure from 1/10th atmosphere to 1 atmosphere brought about the anticipated increase in the percentage of Ammonia formed.

The percentage of Ammonia in equilibrium mixtures of Nitrogen and Hydrogen therefore first falls with rising temperature, in accordance with Haber's results, attains a minimum value, and then rises again until at the temperature of the high tension arc the percentage of Ammonia at atmospheric pressure has increased to a value corresponding on the descending side of the temperature-equilibrium curve with a temperature of about 320°C . The technical synthesis of Ammonia must therefore employ either a low temperature or a very high one. Using a very high temperature, it would be necessary to cool the reaction product very rapidly through the intermediate

temperature range where the percentage of Ammonia in equilibrium mixtures is low and the rate of reaction fast. No attempt has been made to exploit this principle on a technical scale, although Maxted has taken out patents protecting it. Using a relatively low temperature, the difficulty consists in overcoming the high "chemical friction" characteristic of reactions involving combination of gaseous Nitrogen at low temperatures. Even with the most active of known catalysts, the rate of interaction of Nitrogen and Hydrogen is slow below temperatures approaching 500°C ., while catalysts which possess the robustness and resistance to poisons necessary for technical working require generally a still higher temperature. Clearly then, the synthesis of Ammonia is impracticable at atmospheric pressure, since at the temperature necessary for reaction not more than 0.03-0.04 per cent. of combination is realisable per passage over the catalyst. Increasing pressure raises this percentage for any definite temperature, in accordance with the equation

$$[\text{NH}_3] = K[\text{N}_2]^{\frac{1}{2}}[\text{H}_2]^{\frac{3}{2}},$$

where $[\text{NH}_3]$, $[\text{N}_2]$, and $[\text{H}_2]$ represent the concentrations or partial pressures of the gases in question. The value of K for different temperatures can be calculated from data already given.

Preparation of the Gases

One of the most serious difficulties encountered in the technical development of the Ammonia synthesis was due to the rapid poisoning of the catalyst by impurities in the reacting gases. Catalysts vary considerably in their sensitiveness to poisons, but even the most resistant require gases of exceptional purity. Practically complete freedom from Carbon monoxide, water, Sulphur, and Oxygen compounds is vital, since these are powerful inhibitants, and are especially liable to be present in Hydrogen made by either of the usual technical processes. Hence the elaborate processes of purification which must always be employed, and the fact that the cost of Hydrogen accounts for about 75 per cent. of the total cost of synthetic Ammonia.

The Nitrogen is always obtained either directly or indirectly from air. The direct process is one of fractional distillation of liquid air in plant standard for the purpose. The older, the Linde process, is simple, but is not economical of power, and the product contains a considerable proportion of Oxygen. The Pictet process, or its later modifications by Claude, result in a remarkable separation of air into Nitrogen and Oxygen, both approximately pure (see Claude, "Liquid air, Nitrogen and Oxygen," English edition, 1913; and Greenwood, "Industrial Gases," 1920). In the Pictet process, air is cooled by exchange and expansion, and then admitted to the base of a column down which liquid Nitrogen is flowing over plates. This

effects a fractionation of the air, the Oxygen passing into solution in the descending liquid current, while pure Nitrogen passes off at the top. In this way, only about one-fifth of the air used is actually brought into the liquid form, power thereby being saved. A small proportion of the Nitrogen obtained is subsequently liquefied to feed the top of the column, so that separation of Oxygen from the ascending air may be complete, and is brought about in one of two ways: (a) by slight compression of the gaseous Nitrogen in closed coils contained in the liquid Oxygen reservoir, or around the plates of the column, (b) by expansion against external work. Losses due to radiation or imperfect exchange are also compensated by expansion. Fractionation of the liquid also is highly efficient during its descent of the column, so that approximately pure Oxygen collects at the base.

The indirect methods of obtaining Nitrogen from air depend upon removing the Oxygen by combustion. In the Casale, and other processes which owe their success to electrolytic Hydrogen made cheaply by water power, the Oxygen is removed by combination with Hydrogen, sufficient of the latter being employed so that after condensation of the water formed a mixture of Nitrogen and Hydrogen results of suitable composition for the synthesis of Ammonia. Here, modern research is concentrated on evolving the most efficient type of electrolytic cell, to lower the large capital cost of electrolytic plant on the scale required.

When cheap power is not available, the cost of Hydrogen becomes by far the largest single item in the cost of synthetic Ammonia production, and its use for extracting Oxygen from air is therefore inadmissible. Almost always, when the cost of electrolytic Hydrogen is prohibitive, the source chosen instead is water gas, which is treated by the Claude liquefaction process or the B.A.M.A.-G. continuous catalytic process, whereby the Carbon monoxide is replaced by an equivalent of Hydrogen by the action of steam in presence of a catalyst.

When the Hydrogen is required for synthetic Ammonia, Nitrogen in the form of producer gas can be added to the water gas before subjecting to the B.A.M.A.-G. process, as in the Bosch modification, now used exclusively by the Badische Company. In this method, air is burned with coke to give producer gas, consisting of Carbon monoxide and Nitrogen, which is mixed with water gas obtained by the interaction of steam and red-hot coke, and the mixture passed with excess of steam over an activated Iron oxide catalyst. If suitable relative quantities of water gas and producer gas were used initially, the resulting gas, after absorption of Carbon dioxide, consists of Nitrogen and Hydrogen in the proportions approximately of 1 : 3, and is used after purification for the synthesis of Ammonia.

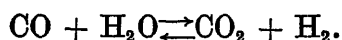
The Nitrogen-Hydrogen mixture can also be made directly by introducing a regulated supply of air into water gas generators during the "making" periods. The effect of this is to combine the water gas and producer gas operations in one plant, possessing the advantage of simplicity, but losing in economy, in that a lower grade fuel can be used for producer gas manufacture (Hembert and Henry, E.P. 1193 of 1884; Read, E.P. 3776 of 1885; Mond and Langer, E.P. 12608 of 1888; B.A.S.F., E.Ps. 26770, 27117, and 27955 of 1912; 8864, 27963 of 1913; F.Ps. 459918, 469907 of 1913; D.R.-PP. 284176, 292615, 293943 of 1913 and 297258 of 1914; E.P. 16494 of 1914; U.S.Ps. 1102716, 1115776 of 1914; 1200805 of 1916; Buchanan and Maxted, E.Ps. 6474, 6476 of 1914; E.P. 14508 of 1920; Harger, E.P. 142874 of 1920; de Jahn and General Chemical Co., E.P. 124760 of 1918; Partington, *J. Soc. Chem. Ind.*, 1921, 40, 99R).

The compositions of water gas and producer gas vary somewhat according to the fuels used, the blast, and other conditions. The mixing is regulated so as to give in the mixture a total of about 70 per cent. "actual" and "potential" Hydrogen, and 23 per cent. Nitrogen: this requiring 2-3 volumes of water gas per 1-2 volumes of producer gas. The approximate percentage compositions are as follows:—

| | Producer gas. | Water gas. | Mixed gas for Carbon monoxide converters. |
|--------------------------|---------------|---------------|---|
| Carbon dioxide . . . | 5 per cent. | 2-6 per cent. | 3-5 per cent. |
| Carbon monoxide . . . | 25 " | 40-45 " | 35-40 " |
| Hydrogen . . . | 5 " | 49-51 " | 33-36 " |
| Nitrogen . . . | 63 " | 0-2 " | 22-23 " |
| Methane, Argon, etc. . . | 2 " | 0 " | 1 " |

At the Badische works at Oppau during the war, 12 gas producers each consuming per day 20 tons of lignite yielded 2 million cubic feet of producer gas. The water gas was made at the same time in 12 generators of the Pintsch type, with rotary grates, 15 feet by 25 feet, each of which gasified 30 tons of oven coke to 3 million cubic feet of water gas per day. The total possible daily output therefore amounted to 24 million cubic feet of producer gas and 36 million cubic feet of water gas, a total of 60 million cubic feet of mixed gases. The plant at Merseburg was even larger.

The mixed gases, made by either of the methods described, are then passed with excess of steam to Carbon monoxide converters, where, in contact with a suitable catalyst, Carbon monoxide is oxidised and an equivalent of Hydrogen formed,



This reaction is really the second stage of the ordinary water gas reaction. Carried out separately, it is possible by using more favourable conditions of temperature and steam concentration to oxidise all but 2 to 4 per cent. of the Carbon monoxide. Thus, the percentage of Carbon monoxide in the equilibrium mixture at various temperatures, and with varying proportions of steam, is shown in the following table:—

| Temp. (°C.). | Volumes of steam per unit volume of gas. | | |
|--------------|--|----------------------|----------------------|
| | 3 vols. | 4 vols. | 5 vols. |
| 400 | 0.45 per cent. of CO | 0.33 per cent. of CO | 0.26 per cent. of CO |
| 450 | 0.8 " " | 0.6 " " | 0.46 " " |
| 500 | 1.25 " " | 0.9 " " | 0.7 " " |
| 550 | 1.8 " " | 1.3 " " | 1.0 " " |
| 600 | 2.45 " " | 1.8 " " | 1.4 " " |
| 650 | 3.2 " " | 2.3 " " | 1.8 " " |
| 700 | 4.05 " " | 2.9 " " | 2.24 " " |

Excess of steam is therefore favourable for conversion, but each additional volume exerts a diminishing effect upon the equilibrium.

At Oppau there were 24 converters, each consisting of two heat interchangers of 30 feet by 15 feet by 6 feet, and a catalyst reaction vessel, 16 feet by 12 feet and 10 feet deep. The whole apparatus was carefully heat-insulated, since with efficient heat conservation the process was completely autothermic. Additional heat was supplied when necessary by adding a little air to the gases, this maintaining the catalyst temperature (400–600° C.) by internal combustion within the catalyst beds. The catalyst consisted of Iron oxide with various promoters, among which, probably, was Chromic oxide, and was supported upon two trays in the catalyst chamber. It retained its activity during two years of continuous working. After passing the catalyst, the gases returned through the heat interchangers, where their heat was transferred to the inpassing gases, to coolers, where excess of steam was condensed.

If it were practicable to carry the reaction to the equilibrium point, less than 2 per cent. of Carbon monoxide would remain in the converted gases. Actually the conversion hardly exceeds 90 per cent., the gaseous product after drying consisting of

| | | | | |
|----------------------|---|---|---|-----------------|
| Carbon dioxide | . | . | . | 27–30 per cent. |
| Carbon monoxide | . | . | . | 2–4 " |
| Hydrogen | . | . | . | 50–52 " |
| Nitrogen | . | . | . | 16–18 " |
| Argon, Methane, etc. | . | . | . | 0.4–0.8 " |

This gas is then subjected to elaborate purification (General Chemical Co., E.Ps. 120546, 124761 of 1918; Lane, E.P. 11878 of 1910; Vignon, F.P. 389671 of 1916; B.A.S.F., D.R.-PP. 282505 of 1913, 289106 of 1914; E.Ps. 8030, 9271, and 15053 of 1914; U.S.P. 1196101 of 1916).

The chief impurity, Carbon dioxide, is removed by scrubbing the gases at high pressure with cold water. The gas from the Carbon monoxide converter, after separating as much water as possible, is compressed in a multi-stage compressor to the pressure of the subsequent reaction, or to some lower pressure, and caused to flow upwards through towers counterwise to a current of cold water flowing downwards over a suitable packing. Carbon dioxide is preferentially dissolved by the descending water, which is discharged at the bottom of the towers through Pelton wheels. The dissolved gases are liberated and much of the power used in pumping the water into the scrubbing towers is recovered.

Efficient scrubbing gives an almost complete separation of Carbon dioxide, as the following compositions show :—

| | Scrubbed gas (percentages). | Gas evolved from the water solution on releasing pressure (percentages). |
|--------------------------|--------------------------------|---|
| Carbon dioxide . . . | 0.1-1.0 | 75-85 |
| Carbon monoxide . . . | 2-5 | — |
| Hydrogen | 68-76 | 8-19 |
| Nitrogen | 22-25 | 4-6 |
| Argon, Methane, etc. . . | 0.4-1.0 | — |

The number of volumes of Carbon dioxide (measured at normal temperature and pressure) which 1 volume of water is capable of dissolving under varying partial pressures of the gas is given in the following table (Wroblewski, *C.R.*, 1882, 94, 1355; Bohr and Bock, *Wied Ann. Phys.*, 1891, 44, (2), 318) :—

| Carbon dioxide pressure (Ats.). | Volumes of gas dissolved at | |
|------------------------------------|-----------------------------|--------|
| | 0° C. | 12° C. |
| 5 | 9.2 | 6.5 |
| 10 | 17.1 | 10.3 |
| 15 | 23.6 | 14.5 |
| 20 | 28.6 | 18.2 |
| 25 | 32.5 | 21.6 |
| 30 | 36.0 | 24.8 |

The residual small quantity of Carbon dioxide left in the washed gases can be removed by scrubbing with a solution of caustic Soda

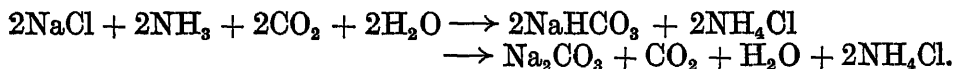
(Soc. L'Air Liquide, E.P. 15053 of 1914), but this is not necessary, since it is extracted in the subsequent treatment which absorbs the Carbon monoxide. The solubility of Hydrogen and Nitrogen involves a loss of about 10 per cent. of these gases, and is unavoidable, being almost independent of the pressure employed. High pressure water scrubbing also effects considerable purification of the gas from other deleterious substances, which are generally present in small quantities, such as Sulphuretted hydrogen.

At the Oppau works of the Badische Company, the gas mixture from the Carbon monoxide converters passes by a 3-foot main to a compressor, which raises it to 25 atmospheres. It is then conducted to the bases of eight steel towers, 30 feet high and 4 feet in diameter, packed with rings, where it is scrubbed by a down-flowing current of water. The water is injected at the top of the towers by circulating pumps, and issues at the bottom, charged with dissolved gases. Here the water and gases pass Pelton wheels, where 60 per cent. of the power used in injecting the water at the top of the towers is recovered. The Carbon dioxide is collected, and used to convert all the Ammonia produced into sulphate or chloride as follows (D.R.-P. 352978 of 1921) :—

Compressed into an aqueous suspension of gypsum, Ammonium sulphate and Calcium carbonate—both useful products—are formed,



The same reaction occurs when an aqueous ammoniacal solution of Sodium chloride is used instead, Ammonium chloride and Soda being the products (the "Ammonia-Soda" process),



About 45,000 cubic feet of Carbon dioxide are obtained per ton of Ammonia synthesised, a much greater quantity than the above reactions can utilise. Methods of applying the gaseous bye-products of the Haber-Bosch process are described by Bosch in *Z. Elektrochem.*, 1918, 24, 361.

After the greater quantity of the Carbon dioxide has been extracted by water scrubbing, the remainder, together with other acid gases, is removed with the Carbon monoxide. If an intermediate pressure has been employed for the water scrubbing, compression is completed up to the intended reaction pressure, and the gases are passed through towers, where they are subjected to the scrubbing action either of a cooled ammoniacal cuprous solution or hot concentrated caustic Soda, or both (B.A.S.F., D.R.-PP. 254043 of 1911; 279954 of 1913; E.P. 1759 of 1912; U.S.Ps. 1126371, 1133087, and 1333087 of 1915).

According to Hainsworth and Titus (*J. Am. C.S.*, 1921, 43, 1), ammoniacal Cuprous chloride is unsatisfactory for large-scale Carbon monoxide absorption, on account of its tendency to deposit Copper and gradually to dissolve the Iron of the containing vessel. These disadvantages are much reduced by using an ammoniacal cuprous salt of an organic acid, such as the carbonate or formate, and an excess of at least 6 per cent. of free Ammonia. The capacity of ammoniacal solutions of Cuprous carbonate to dissolve Carbon monoxide depends upon the concentration of free Ammonia and of cuprous Copper, as well as upon the partial pressure of the Carbon monoxide. A minute proportion of Oxygen in the gases is stated to prevent any reduction to metallic Copper, and rather to increase the efficiency of the absorbent. Since a dissociable compound, probably $\text{Cu}_2(\text{NH}_3)_2\text{CO}_3 \cdot 2\text{CO} \cdot 4\text{H}_2\text{O}$, is formed, absorption of Carbon monoxide by ammoniacal cuprous salts is not as a rule complete.

The effect of scrubbing gases at high pressure with an ammoniacal solution of a cuprous salt is to reduce the Carbon monoxide to a very small percentage, and completely to eliminate Oxygen, and acid gases (such as Carbon dioxide, Hydrogen sulphide) by combination with the Copper, or the Ammonia respectively. The gas after such scrubbing may contain the following percentages of impurities :—

| | | | | |
|----------------------|---|---|---|------------------|
| Carbon monoxide | . | . | . | 0.01 to 0.1 |
| Ammonia | . | . | . | Variable traces. |
| Water vapour | . | . | . | 0.03 or less. |
| Methane, Argon, etc. | . | . | . | 1.0 |

The spent ammoniacal cuprous solution, after release from the bottom of the scrubbing towers, passes to regenerating apparatus, where the Carbon monoxide is continuously removed by heating *in vacuo*. The Carbon monoxide cuprous complex decomposes at 70° C. and the gas is collected while the solution is readjusted for repeated use.

Many proposals have been made for removing the Carbon monoxide as formate, by scrubbing with hot concentrated caustic Soda solution, either as an alternative to the Cuprous ammonium method, or in addition. According to Weber (Dissertation, Karlsruhe, 1908) and Fonda (Dissertation, Karlsruhe, 1910) the optimum conditions for absorption of Carbon monoxide by caustic Soda are a temperature of 200° C. and a concentration of alkali of 10 per cent., these conditions reducing the concentration of Carbon monoxide to less than 1 per cent. The General Chemical Company, Sheffield, Alabama, in their plant erected under the auspices of the United States Government, endeavoured to apply this method to the separation of the greater part of the Carbon monoxide, removing the remainder

by means of an ammoniacal cuprous solution (Tour, *J. Ind. Eng. Chem.*, 1920, 12, 844). Insuperable mechanical difficulties, due especially to separation of insoluble Sodium carbonate, led to the abandonment of caustic Soda absorption, and the use instead of ammoniacal Cuprous carbonate only, which, however, did not yield a gas of sufficient purity, having regard to the catalyst employed. The Badische plants at Oppau and Merseburg, be it noted, absorb the major bulk of the Carbon monoxide by means of ammoniacal Cuprous formate solution, and complete the elimination by the use of caustic Soda of 25 per cent. concentration at 260° C.

At Oppau, the gas from the Carbon dioxide water scrubbers passes first through steel bottles, which serve as spray catchers to the high pressure system. Here it is compressed to 200 atmospheres and delivered to 16 towers, each 25 to 30 feet high and 30 inches internal diameter, packed with balls. They are constructed in one piece, of a special steel, with flanged ends for bolting in position. ammoniacal Cuprous formate solution is circulated in the first eight, and 25 per cent. caustic Soda solution maintained at 260° C. in the remaining eight. Circulation of the liquids is effected by eight hydraulic pumps, made of forged steel. The ammoniacal Cuprous formate solution absorbs up to 10 times its volume of Carbon monoxide, and after discharge at the bottom of the absorbing towers is regenerated by flowing down a warmed and partially evacuated tower 40 feet high. The Carbon monoxide which is released is passed to the Hydrogen contact plant, while the cuprous solution is readjusted and used again.

After the treatment described, the only additional purification that is necessary, given a catalyst of satisfactory properties, is the removal of water. This is effected by refrigeration at high pressure, followed by passage over a desiccating agent, such as Soda-lime, or Sodamide. The Badische works at Merseburg, after purifying the gas mixture as at Oppau, complete the elimination of catalytic poisons by passing through a series of small catalyst furnaces before leading the gases to the main furnace (E.P. 5835 of 1911; see Partington, *J. Soc. Chem. Ind.*, 1921, 40, 144).

The use of a "protector" furnace for final elimination of catalytic poisons has been widely recommended. Claude has adopted it, using spent catalyst. It has also been suggested to remove the last traces of Carbon monoxide from Hydrogen by passage over metals, such as Iron or Nickel, under hydrogenating conditions (see, for example, E.P. 131049 of 1918).

The mixture of Nitrogen and Hydrogen, made and purified in the way described, should contain approximately 1 volume of the former per 3 volumes of the latter. Correct adjustment of these proportions is essential, since in the synthesis they are removed in

these proportions, and any disproportion originally increases as combination proceeds. The most convenient procedure is to supply to the circulation a mixture containing a slight excess of Hydrogen and periodically adjust the composition of the circulating gases by addition of the requisite amount of pure Nitrogen obtained from a Linde or Pictet machine (B.A.S.F., D.R.-P. 265295 of 1912; U.S.P. 1075085 of 1913).

In the Claude process, Nitrogen is obtained by fractional distillation of air by modified Pictet plant, as already described. For Hydrogen, Claude has worked out a method of separation from water gas, and more recently from coke-oven gas, depending upon the removal of impurities by fractional liquefaction. After stripping in an ordinary bye-product plant, the coke oven gas is compressed to 25 atmospheres, and passed through towers counter current to a stream of cold water to dissolve out the Carbon dioxide. Last traces of Carbon dioxide are then extracted by lime water. Unless all the Carbon dioxide is removed it solidifies in the next stage of the process, in which the compressed gas is progressively cooled in ascending a column. Ethylene and higher hydrocarbons first condense, then Methane, then the Carbon monoxide, and finally the Nitrogen, leaving only the Hydrogen. The Nitrogen, liquefying last, at the top of the column, runs down, and in so doing scrubs out the last of the other gases which are soluble in liquid Nitrogen. The issuing Hydrogen is expanded in an engine while doing external work and is thereby cooled to -210°C . The cold Hydrogen then traverses a heat interchanger in counter current to the untreated coke oven gases on their way to the liquefaction apparatus. The Hydrogen obtained is free from all catalytic poisons except 2 per cent. or less of Carbon monoxide, which is removed later either by absorbents or by use of a "protector" catalyst. Claude's method of lubricating the cylinder of his expansion engine is simple. Ordinary lubricants for low-temperature apparatus, such as petroleum ether, which freezes at -90°C ., are useless. Small quantities of Nitrogen are left with the Hydrogen, the presence of which is harmless, having regard to the purpose for which the Hydrogen is required, and this, liquefying in the cylinder, forms an excellent lubricant.

The liquefied gases are burnt in gas engines for the production of power. By limiting the supply of air to the engine, the exhaust gas, after removal of the Carbon dioxide and water, is mostly Nitrogen, which, after purification, it is suggested, may be used in the process (West, "The Claude Process," *J. Soc. Chem. Ind.*, 1921, 40, 420R; see also Ellis, U.S.P. 1327029).

Claude has also proposed to obtain Hydrogen for synthetic Ammonia from water gas or coke oven gas by compressing to about

100 atmospheres and cooling to about -50° C. in presence of an organic solvent such as Ether, which dissolves Carbon monoxide and other gases more easily than Hydrogen. Using a scrubbing tower, less than 0.2 per cent. of Carbon monoxide remains in the products. Greater compression or further cooling results in a larger proportional loss of Hydrogen (*C.R.*, 1921, 192, 974). Brunner Mond and Co. and de Jahn (E.P. 215789 of 1924) and Cederburg and the Norsk Hydro-Elektrisk (U.S.P. 1478889 of 1923) suggest a scrubbing of the gases at high pressure and low temperature with liquid Ammonia.

A modification of the "intermittent method" (the alternate action of steam and water gas upon Iron) is stated by Maxted to give Hydrogen free from Carbon monoxide, and pure as the electrolytic gas (*J. Soc. Chem. Ind.*, 1917, 36, 779). As usually carried out, Carbon monoxide always occurs in the product, since during the reduction periods, at the high temperature necessary, some of this gas reacts as follows:—



The Carbon is deposited upon the Iron and gives Carbon monoxide in the succeeding steaming period. Maxted's modification consists in employing for the reduction water gas containing a considerable percentage of Carbon dioxide, which prevents deposition of Carbon, and makes it possible to obtain directly Hydrogen of 99.9 per cent. purity.

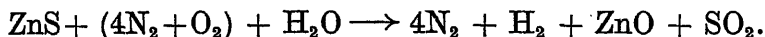
West proposed to make Hydrogen by combining the water-gas reactions and the distillation of coal in coke ovens (*J. Soc. Chem. Ind.*, 1922, 41, 393R) as follows: Coal is distilled in a retort, and water gas made from the resulting coke. Nearly all the Hydrogen in coal is liberated as such if the crude coal gas is passed through the hot zone of a gas producer, or water-gas generator, all hydrocarbons "cracking" into Carbon and free Hydrogen. The Carbon so formed, together with the coke, then interacts with steam, to produce water gas, consisting of 50 per cent. Hydrogen and 42 per cent. Carbon monoxide. The combined water gas and coke oven gas are then treated according to Claude's liquefaction process, or passed with excess of steam over activated Iron oxide to effect the second stage of the water gas reaction. In this way, coal can be completely gasified, yielding all its Hydrogen as such, while the Carbon sets free its equivalent of Hydrogen from steam (see also Harger, E.P. 142874).

Many patents have appeared in which the use of crude industrial gases containing Nitrogen, oxides of Carbon, and Hydrogen have been suggested for the manufacture of a suitable mixture of Nitrogen and Hydrogen. Such gases, either alone or mixed with water gas, are passed with excess of steam over an activated Iron oxide catalyst,

and the resulting mixture is purified and adjusted to the required proportions as before (for example, B.A.S.F., E.P. 145058 of 1920).

Other methods depend upon the cracking of hydrocarbons, or gas oils, in presence of air and steam. In contact with a suitable catalytic surface at a high temperature, the products are entirely gaseous, consisting of Nitrogen, Hydrogen, oxides of Carbon, and water vapour, which can be treated in the way described (*e.g.*, Nitrogen Corporation, E.P. 163047 of 1921, U.S.P. 1425579).

Various proposals have also been put forward for making Nitrogen and Hydrogen simultaneously with Sulphur dioxide, by passing air or water vapour, either separately or together, over roasted metallic sulphides, such as pyrites or blendes (E.P. 143854, D.R.-P. 340753),



The interaction of Sulphur vapour and steam at 800° C. has been proposed by Clancy and the Nitrogen Corporation (E.P. 163323 of 1921), who separated the resulting Sulphur dioxide from the Hydrogen by absorption in aqueous Ammonia, then oxidising the Ammonium sulphite formed to sulphate.

The numerous older processes available for manufacture of Hydrogen and Nitrogen (see Greenwood, "Industrial Gases," London, 1920) are economically impossible from the point of view of synthetic Ammonia.

Catalysts

Very many patents have appeared protecting the use of metals and their compounds as catalysts, but comparatively few have proved suitable for technical use. For a short time, with pure gases, a large number of substances are highly active, but long catalytic life under technical conditions is difficult to attain, mainly on account of sensitiveness to poisons. The active metal catalysts are the alkali and alkaline-earth metals, those related to Iron, and those of high atomic weight, such as Molybdenum, Tungsten, Uranium, and the Platinum metals. The activity of these metals is often greater when they are used in the form of compounds containing Carbon, Nitrogen, or Hydrogen (Carbides, Nitrides, or Hydrides), or when they have been prepared in a way that such compounds may be present (*e.g.*, from Cyanides or complex Cyanides), while carbonitrogenous metallic compounds, so long as Sulphur is absent (*e.g.*, Cyanides, Cyanamides, or Amides of metals), are active catalysts in themselves.

Anticatalysts for this reaction are Sulphur in any form, Oxygen and its compounds, especially water and Carbon monoxide, compounds of Selenium, Tellurium, Boron, Phosphorus, Arsenic, Antimony, and metals of low melting point whose oxides are reduced by

Hydrogen, especially Bismuth, Lead, Tin, and Zinc. Carbonaceous substances also are anticatalytic, so that lubricating oil must be avoided. It is the custom to arrange for the lubrication of all internal parts of the apparatus with liquid Ammonia.

The variety and number of these poisons have been the chief difficulty in the way of technical success. Commercial Iron is quite inert as a catalyst, and Haber has shown that 0.01 per cent. of Sodium sulphate in pure Iron is seriously harmful, while 0.1 per cent. of Sulphur in any form renders it useless (*J. Soc. Chem. Ind.*, 1912, 31, 982). If, however, commercial Iron is burnt in Oxygen, anticatalytic impurities are destroyed, and the oxide so obtained, when reduced in Hydrogen below 500° C. and cooled in a current of Ammonia, is a highly active catalyst.

Catalysts vary considerably in their sensitiveness to poisons. Since changing the catalyst and recommencing the operation of large scale Haber plant require several days and expert manipulation, long life of the catalyst, and therefore maximum resistance to poisons, is essential. Many catalysts have been proposed which, it is claimed, combine a high activity with a relatively low sensitiveness to poisons, but it would appear that the only successful ones (such as those employed by the Badische Co., by Synthetic Ammonia, Ltd., and by Claude) consist of Iron, activated by addition of certain promoters, taking advantage of the cumulative action of two or more promoters present together.

Ammonia catalysts are as susceptible to the influence of promoters as they are to the effect of poisons. The substances most commonly referred to as promoters in the patent and other literature (generally for an Iron catalyst) are the metals Chromium, Molybdenum, Tungsten, Uranium, Cobalt, and Nickel. It is noteworthy that these metals form nitrides, some of them under the conditions of working, a fact which perhaps explains why a current of pure Hydrogen and pure Nitrogen can be employed alternately, instead of mixed. Small quantities of alkali or alkaline-earth oxides or hydroxides also promote the action, as well as oxides of rare-earth metals, and certain other oxides and salts which are not reduced by Hydrogen. For this reason, pumice, or supports containing Magnesia, Alumina, or Magnesium carbonate have often been recommended (E.P. 127025 of 1917, D.R.-P. 289105, etc.; see also B.A.S.F., Claude, Casale, Clancy, and Cederburg patents).

It is impossible here to enter into the very voluminous patent literature concerning catalysts for synthesis of Ammonia. Most of the information is vague, and much entirely misleading. The following account is intended to indicate catalysts that have at different times been used, or considered for use, on a technical scale.

Among the first catalysts investigated by Haber were Osmium

and Uranium, both of which were found to be very active, the latter especially so in the form of its carbide. Both gave a perceptible reaction velocity at 350°C ., and very rapid action at 550°C . Osmium, however, could not be considered for technical use on account of expense and inadequate supply, while Uranium compounds were too susceptible to poisons, especially water and Oxygen compounds. Molybdenum and Tungsten also were found to be powerful catalysts, the former as metal, Molybdic acid, Ammonium molybdate, or Molybdenum nitride, and the latter as metal or Nitride, the preparations in each case being made in a current of Ammonia, or Ammonia under pressure, and at a temperature not greatly exceeding 550°C . The alkali and alkaline-earth metals and their amides, as well as Manganese, were strongly active so long as Oxygen compounds and water were rigorously excluded, and the rare-earth metals, and Cerium, Niobium, Tantalum, etc., were also used. Iron was ultimately selected, since, though it required a higher temperature for its action than many of the other catalysts, this was more than compensated for by its longer active life.

All metal catalysts can be satisfactorily prepared by decomposition of appropriate nitrates, reducing the oxide so formed in a current of Hydrogen or Ammonia, preferably in the catalytic furnace subsequently to be employed, and sometimes using the reducing gas under high pressure. Alternatively, the oxides may be made by precipitation, but sulphates must be avoided on account of the poisonous action of Sulphur in any form.

The Badische Company use an activated Iron catalyst. The promoters employed are a well-kept secret, but there is reason for suspecting the use of Molybdenum or Chromium, or both (see D.R.-P. 265295 of 1912; U.S.P. 1188530 of 1916).

The process worked for a short time at the United States factory, Sheffield, Alabama, employed an activated Sodamide catalyst, made somehow as follows (U.S.Ps. 1141947, 1141948, and 1143366 of 1915, and 1159364). Pumice was impregnated with Iron or Nickel nitrate, heated to 550°C ., and the oxide reduced. Sodamide was then deposited upon the spongy metal by treating with melted Sodium and Ammonia gas at 450°C . Such a catalyst was said to operate at 500°C . and 70 atmospheres, but it was too susceptible to poisons, especially water and Carbon monoxide, and the process employing it was abandoned.

The catalyst employed in the Claude process is an activated Iron, made by burning commercial Iron in Oxygen, adding to the oxide so formed promoters which have the effect (it is claimed) of immunising the Iron against the action of poisons, and reducing the whole with Hydrogen in the catalyst reaction chamber. The following particulars are given (E.P. 153254 of 1921). Iron is melted and

raised to a very high temperature by a strong jet of Oxygen directed upon the metal heated in a magnesia crucible. Some of the Magnesia dissolves in the resulting oxide, which when cast and granulated is an active catalyst, but of short life. If, however, 5–10 per cent. of Calcium oxide with a little alkaline oxide be added during the Oxygen blast, then the catalyst so formed is good for some hundreds of hours.

An activated Iron or Iron oxide catalyst made in a similar way to that recommended by Claude is also used in the Casale process (E.Ps. 197199 of 1922, 218237 of 1923; Canadian P. 229485 of 1923). Oxygen under pressure is injected into metal turnings, consisting of Iron, or an alloy of Iron with Molybdenum, Tungsten, Uranium, Manganese, or Chromium, heated in a Magnesia crucible. The oxide which is rapidly formed melts, and the blast of Oxygen is continued until the violent ebullition which sets in has caused 5 to 15 per cent. of the oxidation product to vaporise away, eliminating all detrimental impurities. The product is then allowed to cool, is crushed, and reduced in Hydrogen or Nitrogen–Hydrogen mixture as most convenient.

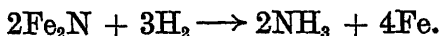
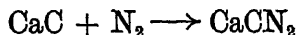
Iron oxide catalysts, with promoters incorporated by fusing and dissolving, are also recommended by Larson and Richardson (*J. Ind. Eng. Chem.*, 1925, 17, 971), and a practical method is described for preparing them.

According to E.P. 227491 of 1923, Casale heats the artificial or mineral oxides of Iron or related metals (Cobalt, Nickel, Manganese, Molybdenum, Tungsten, and Uranium) with another substance, such as Carbon, Magnesium, Aluminium, or Calcium, whose oxide has a high heat of formation. To obtain a yet higher temperature, the Oxygen blast may be employed. The mechanical properties of the product obtained are very suitable for catalytic purposes, and the Magnesia, Lime, or Alumina which is present combines the functions of support and promoter.

Clancy and the Nitrogen Products Corporation have directed attention to the following types of catalysts:—

1. Cyanamides, especially of the alkali and alkaline-earth metals, Copper and Manganese, either alone, or associated with a finely-divided metal (E.Ps. 128939, 140439, 143550 of 1920; U.S.Ps. 1252174, 1252178 to 1252182; and Canadian Ps. 216515 to 216521 of 1922). Cyanamides are useless at ordinary pressure, owing to their decomposition into Hydrocyanic acid, which, however, does not occur in presence of Nitrogen and Hydrogen at high pressures, the Cyanamide then acting as a true catalyst. A metal that forms a not too stable nitride, such as Iron, Cobalt, Manganese, Ruthenium, Osmium, Niobium, or Tantalum, added in a finely-divided form, greatly influences the action of the Cyanamide, so that relatively low

temperatures of reaction, *e.g.*, 400–600° C., are possible, and such mixtures, moulded into porous briquettes, provide very good catalysts. Examples are CaCN_2 (50), Iron (10), and Manganese (10), or MnCN_2 (10), NaCN_2 (100), and CoCN_2 (10). The following series of reactions was assumed to occur :



The carbides of Calcium, Barium, or Potassium instead of the cyanamides may naturally be substituted, or the nitrides of Iron and Manganese in place of the free metal.

2. Iron, Manganese, and Chromium catalysts, containing also an alkali or alkaline-earth metal, together with combined Carbon and Nitrogen, are made by heating a double cyanide of the metal and an alkali or alkaline earth (preferably Potassium or Calcium) to 400° C. in presence of Ammonia (E.Ps. 155592, 156698 of 1921; U.S.Ps. 1363392–3, 1439291–2, 1454599 of 1923; Canadian P. 226262 of 1922). A concentrated solution of the double cyanide in water is evaporated with pumice granules in an inert atmosphere, and the impregnated pumice heated at 400° C. in Ammonia gas, preferably under pressure.

The method of U.S.Ps. 1483412 and 1483414 prepared Cyanamide and Cyanide catalysts as follows: An alkali or alkaline-earth hydroxide or carbonate is mixed with charcoal or activated Carbon, and a metal, such as Iron, Manganese, Chromium or Cobalt, or an oxide or a carbonate of one of these. The fine powder obtained is mixed to a paste with water, made into briquettes, dried, and then heated at a temperature well above 500° C. in a current of pure Nitrogen at high pressure. A mixture of alkali or alkaline-earth cyanides or cyanamides is formed, the Iron or other metal acting in this reaction catalytically. The briquettes are then rendered porous by soaking in liquid ammonia and heating to 450° C. in a current of Nitrogen and Hydrogen.

Similar results are attained in another way in the methods of E.Ps. 179155 and 180314 of 1922, or U.S.Ps. 1473543–4. Cyanamides or Cyanides of alkali or alkaline-earth metals, or of Beryllium or Magnesium, are made by heating the carbonate, formate, acetate, oxalate, tartrate, or phenolate to 500° C. in presence of Ammonia gas at 100 atmospheres. The products are active catalysts at 500° C. Some advantage is gained by mixing with the organic salts a finely-divided metal, such as Iron, Cobalt, Manganese, Thorium, or Uranium, or an oxide, a hydroxide, carbonate or an organic salt of one of these metals.

Cederburg and the Norsk Hydro-Elektrisk also employ catalysts prepared from simple or complex cyanides, especially of Iron, Cobalt, Nickel, or Chromium. They especially recommend Iron catalysts made from a complex cyanide with an alkali metal in which 2 molecules or less of alkali cyanide are present per molecule of Iron cyanide, e.g., $(\text{NH}_4)_3\text{KFe}(\text{CN})_6$ or $\text{K}_2\text{Fe}_2(\text{CN})_6$. When these are decomposed by heating below 500°C ., they are stated to yield catalysts active at 400°C . (E.P. 153290 of 1920; U.S.P. 1452027 of 1923; Canadian Ps. 219825 and 223453 of 1922).

In the method of E.P. 168902 of 1921, a soluble ferrocyanide, for example, $\text{K}_4\text{Fe}(\text{CN})_6$, is precipitated with a soluble metallic salt (Ferric chloride may be used), and the insoluble ferrocyanide, or Prussian blue so obtained after washing free from soluble Iron salts, is dried and heated in an inert atmosphere.

The Separation of Ammonia

The Ammonia formed at each contact of Nitrogen and Hydrogen mixture with the catalyst is extracted by one of the two following methods:—

1. *Liquefaction.* The proportion of Ammonia formed is sufficient to exert a partial pressure considerably greater than the vapour pressure of liquid Ammonia at the ordinary temperature. Refrigeration therefore causes condensation of a large proportion of the Ammonia formed at each contact (General Chemical Co., E.P. 120546 of 1918; B.A.S.F., D.R.-PP. 235421 of 1908, 259996 of 1911, 270192 of 1912, and U.S.P. 1202995 of 1916).

2. *Solution in cold water.* (B.A.S.F., D.R.-PP. 235421 of 1908; 270192 of 1912; F.P. 458951 of 1913; E.Ps. 25260 of 1912 and 9654 of 1913).

The theoretical efficiencies of these two methods are shown in the following tables, in which the vapour pressures of Ammonia over (a) liquid Ammonia, (b) a 25 per cent. aqueous solution of Ammonia are shown for various temperatures (Perman, *J.C.S.*, 1903, 83, 1169):—

| Temp. $^\circ\text{C}$. | Vapour pressure of NH_3 over liquid NH_3 (ats.). | NH_3 in gas at 200 atmo- spheres (per cent.). |
|--------------------------|---|---|
| 0 | 4.2 | 2.1 |
| -10 | 2.8 | 1.4 |
| -20 | 1.8 | 0.9 |
| -30 | 1.2 | 0.6 |
| -40 | 0.7 | 0.34 |
| -50 | 0.4 | 0.2 |
| -60 | 0.2 | 0.1 |

| Temp. °C. | Vapour pressure of 25% NH ₃ solution (ats.). | | Volumes in gas at 200 ats. (per cent.). | |
|-----------|---|--------|---|--------|
| | NH ₃ . | Water. | NH ₃ . | Water. |
| 0 | 0.2 | 0.003 | 0.1 | 0.0015 |
| 10 | 0.3 | 0.007 | 0.15 | 0.0035 |
| 20 | 0.45 | 0.013 | 0.2 | 0.0065 |
| 30 | 0.7 | 0.027 | 0.35 | 0.0135 |
| 40 | 1.05 | 0.055 | 0.5 | 0.0275 |

1. *Liquefaction.* The gases from the converter, charged with Ammonia, pass first through heat interchangers, and then, just before arriving at the liquefaction coils, through a cold interchanger. Ammonia condenses in the coils, which are refrigerated externally, and is removed by mechanical separators, while the uncondensed gases, containing relatively little Ammonia, pass on, *via* the cold interchanger, to repeat the cycle.

The efficiency of this mode of separation of Ammonia depends upon either a high conversion by the catalyst or the use of a very low temperature in the refrigerated coils. Thus, if the catalyst delivers to refrigerated coils at -20° C. gas containing not more than 4 per cent. of Ammonia at 100 atmospheres, then nearly half the Ammonia fails to be condensed. A lower limit of temperature for the refrigerator is imposed by the freezing point of Ammonia, about -75° C. Separation by cooling has the advantage of avoiding contamination of the circulating gases with water, and has been tried by the Badische Company, and by the General Chemical Company of America, who, however, appear to have abandoned it in favour of water solution. In Claude's process, on the other hand, employing a very high pressure, and obtaining therefore conversions of 40 per cent. at each passage over the catalyst, separation of the Ammonia by liquefaction, using only water cooling, has become a distinctive feature.

2. *Solution in Cold Water.* Separation of Ammonia can be rendered as complete as desired, and any concentration of Ammonia in water can be obtained by scrubbing the circulating gases with cold water in a suitable apparatus. Much heat is liberated in dissolving, so that the process is best carried out in several stages, with external cooling. Small water scrubbing towers, packed with suitable material and sufficiently strong to withstand the pressure of the circulating gases, can be used, but, better, water-cooled coils through which the gases and water circulate in opposite directions. At the high pressure, considerable quantities of Nitrogen and Hydrogen dissolve in the scrubbing water, which is discharged into a low-pressure receiver at the bottom of the scrubbing apparatus. A

strong solution of Ammonia is collected, while the gases passing from it, consisting of Nitrogen, Hydrogen, and Ammonia, are separately caught, the Ammonia in a water scrubbing tower and the Nitrogen and Hydrogen in storage gasometers for the gas mixture.

At the Oppau works of the Badische Company, three water injector pumps supply nine sets of absorbers. Each absorbing set consists of three water-cooled steel spirals set vertically, through which the water flows from top to bottom. The gas is first admitted to the top of the lowest spiral, down which it flows. At the bottom it is conducted to the top of the middle spiral, and, after passing down this, to the top of the uppermost spiral. The flow of gas and absorbent is therefore concurrent in each individual spiral, but counter-current with regard to the three. After circulating through the absorbing system, the gases are thoroughly dried before the next contact with the catalyst, towards which water exerts a strongly anticatalytic influence. The Ammonia solution collected is about 25 per cent. concentration, and is discharged through an expander. The Ammonia there liberated is absorbed in water in a tower, while the Nitrogen and Hydrogen pass back to the gasholder, where they are used again.

After separation of Ammonia by solution in water, the circulating gases must be thoroughly dried and deprived of any traces of Oxygen that may have gained entry, dissolved in the water, or otherwise. This is effected by refrigeration, or by a desiccating agent, to remove the water, and a "protector" furnace to combine the Oxygen.

The Haber Process

In the Haber process, and its British, American, Italian, Norwegian, and other modifications, a mixture of 1 volume of Nitrogen with 3 volumes of Hydrogen at high pressure is circulated over a catalyst maintained at a temperature between 500° C. and 600° C., for the most part by the heat of reaction (Haber, E.P. 14023 of 1910; D.R.-PP. 229126, 238450 of 1909; U.S.Ps. 971501 of 1910, 999025 and 1006206 of 1911, 1202995 of 1916; B.A.S.F., D.R.-PP. 235421 of 1908 and 259996 of 1911. Haber and collaborators, *Chem. Zeit.*, 1910, 34, 345; *Z. Elektrochem.*, 1910, 16, 244; 1913, 19, 53; 1914, 20, 597; 1915, 21, 191; *J. Soc. Chem. Ind.*, 1913, 32, 134; 1914, 33, 49).

The lower the working temperature the more favourable is the equilibrium for formation of Ammonia, but this advantage is offset in practice by the slowness of the reaction at temperatures below 500° C. Even at this temperature only an extremely active catalyst induces a rate of reaction fast enough to effect a satisfactory conversion. At each transit over the catalyst a certain percentage of

the passing gases is combined to Ammonia, this proportion depending upon the pressure, temperature, and activity of the catalyst, and the time of contact (or rate of circulation).

Except when a slow rate of circulation is employed, the conversion at each passage is less than that theoretically possible—that is, the amount corresponding with the equilibrium concentration under the ruling conditions of temperature and pressure. In order that Ammonia may be produced continuously, after each passage over the catalyst the Ammonia formed is extracted, and the unchanged gases are recirculated, with fresh Nitrogen and Hydrogen added to re-establish the pressure, making up for that withdrawn. Unless the Ammonia is removed as completely as possible between each transit of the gases over the catalyst, the rate of production sinks, since equilibrium is attained in the next contact with a smaller amount of fresh gases combining. Such a result may have far-reaching consequences, since less combination involves less generation of heat, which may upset the delicately adjusted thermal balance of the process.

The properties of the reacting substances and the conditions of the reaction impose, as we shall see, certain severe limitations in regard to the construction of the catalytic furnace and the materials of which it is composed. These have the effect of rendering very difficult any considerable addition of heat from external sources to the catalyst (see D.R.-PP. 259870 of 1911 and 268929 of 1912). In all plants successfully operating the Haber process, the reaction is therefore almost or quite autothermic. To attain this thermal balance, a catalyst of very high activity is vital, so that sufficient combination of Nitrogen and Hydrogen continuously takes place to offset by the heat of reaction thermal losses due to radiation and imperfect exchange.

The Haber process is usually carried out at about 200 atmospheres pressure and a temperature of 500–650° C., under which conditions a theoretical conversion of 8–11 per cent. is possible at each contact. In practice, the conversion may reach 7–9 per cent., and for this small proportion of combination to supply the necessary heat, heat exchange must be efficient, the separation of Ammonia after each transit of the catalyst almost complete, so that maximum union may occur at the next contact, while the rate of circulation must be uniform and easily adjustable, since upon this depends the control of the other factors. Heat interchange between gases can be made extremely efficient at high pressures—the higher the pressure the more rapid is the transfer of heat towards the point of thermal equilibrium. It will be seen that the variables of the process, namely, the catalyst activity and its temperature, the efficiency of heat interchange and Ammonia separation, and the pressure and rate of circulation of the

gases, are interdependent, and that regularity of each is essential for a high rate of production and autothermic working.

The choice of catalyst has always involved considerable difficulty. However efficient the constructional details of the furnace and circulation, unless the catalyst is well chosen, both in regard to resistance against poisons and high activity, satisfactory working will not be achieved. The advantage of the catalyst activity is secured in two ways, both of which increase the rate of production and tend to render the process more completely self-sustaining. Thus with an active catalyst, (1) a convenient rate of reaction is induced at a lower temperature, where the equilibrium of the reaction is more favourable, (2) a faster rate of gas flow can be employed.

The rate of production of Ammonia = amount formed per contact \times number of contacts per unit of time. The upper limit of magnitude of these factors can only be reached with a catalyst of maximum activity, and with the other variables uniform and properly adjusted, which, in turn, depends upon the regular and efficient working of each part of the circulation. For the maximum rate of production it is not necessary to obtain equilibrium during contact with the catalyst, but a conversion sufficient to maintain the thermal balance, increasing the rate of gas flow to a maximum consistent with this.

In operation, the withdrawal of Nitrogen and Hydrogen as Ammonia leads to an accumulation of inert gases, mainly Argon and Methane, in the circulation. This accumulation is balanced by incidental leakage, permeability of metal by gas at a high temperature, and a regulated discharge, whereby some 10 per cent. of the Nitrogen and Hydrogen are rejected. This gas "purge" has the effect of keeping the proportion of circulating inert gases down to about 5 per cent. The overall yield of Ammonia in operating Haber plant over a long period is said to be about 80 per cent. of theory, calculated on the quantity of gas mixture consumed.

The Catalyst Reaction Bomb. Externally heated furnaces as used at first were quickly abandoned on account of the action of hot Hydrogen and Ammonia at high pressures on the steel walls. At such a temperature as the reaction requires—a red heat—most metals are more or less permeable to Hydrogen, while steel is rapidly decarbonised, Hydrogen at high pressure reacting with the Carbon to produce Methane, while Ammonia also has some action. The effect is dangerously to weaken the metal and render it porous, while its tensile strength is already greatly reduced at temperatures above 400° C. In early types of furnace, attempts were made to counter these disadvantages by enclosing the catalytic furnace in a large envelope containing Nitrogen at the pressure of the process, or somewhat higher—a cumbersome device, and not very effective.

All recent types of furnace are constructed of special alloy steel, containing only a small proportion, if any, of Carbon. Chromium, Tungsten, and Vanadium steels, containing also a percentage of Nickel, have been found most satisfactory for withstanding the extremely rigorous requirements of the process. The Badische patents (D.R.-PP. 291582, 298199, 306333; E.Ps. 29260 of 1912, 13258 of 1913) state that steels containing these metals are suitable, even if much Carbon is present, their strength being largely retained even on decarbonisation by the high-pressure Hydrogen. Much Nickel should be avoided, unless large quantities of the alloying metal are also present. A steel which is stated to be satisfactory contains 5 per cent. of Tungsten and 5 per cent. of Nickel (see also B.A.S.F., D.R.-PP. 254571, 256296, 265295 and 275156 of 1911-12; U.S.Ps. 1075085 of 1913, 1188530 of 1916).

According to Ernst, Reed, and Edwards (*J. Ind. Eng. Chem.*, 1925, 17, 775) a Chrome-Vanadium steel is most resistant in which the ratio of Carbon to Chromium is not greater than 1 to 8. The tensile qualities are not appreciably improved by increasing the Chromium content above 2.5 per cent., so that metal for parts of the furnace in contact with hot reducing gases may consist of an alloy containing 2.5 per cent. of Chromium, 0.18-0.20 per cent. of Vanadium, and 0.3 to 0.35 per cent. of Carbon, while other parts can be made of 3 per cent. Nickel steel.

The tensile strength and other desirable properties even of such steels commence to fall at temperatures above 250-300° C. It is understood, however, that recently Messrs. Vickers, of Sheffield, have produced a steel which is both highly resistant and maintains its tensile properties almost unimpaired, even at a low red heat.

On account of the effect of temperature on all steels hitherto used, not only must carefully selected material be used in construction of the furnace, but the arrangement must be such that the pressure-sustaining walls are not subjected to the full heat of the reaction. This is achieved by internal heating of the catalyst, mainly by heat interchange and the heat of reaction, making up any small deficiency by an electrical resistance coil heating the catalyst, or preheating the gases, while the pressure-resisting walls are protected from overheating by the cold incoming gases entering the peripheral regions of the furnace, between the pressure-resisting walls and the sources of heat. In many furnaces, heat interchange also is internal, the gases after passing by the inner face of the furnace wall arriving at coils or tubes conveying the hot gases from the catalyst.

One of the later experimental types of furnace used by Haber is shown in Fig. 15, and the completed circulation diagrammatically

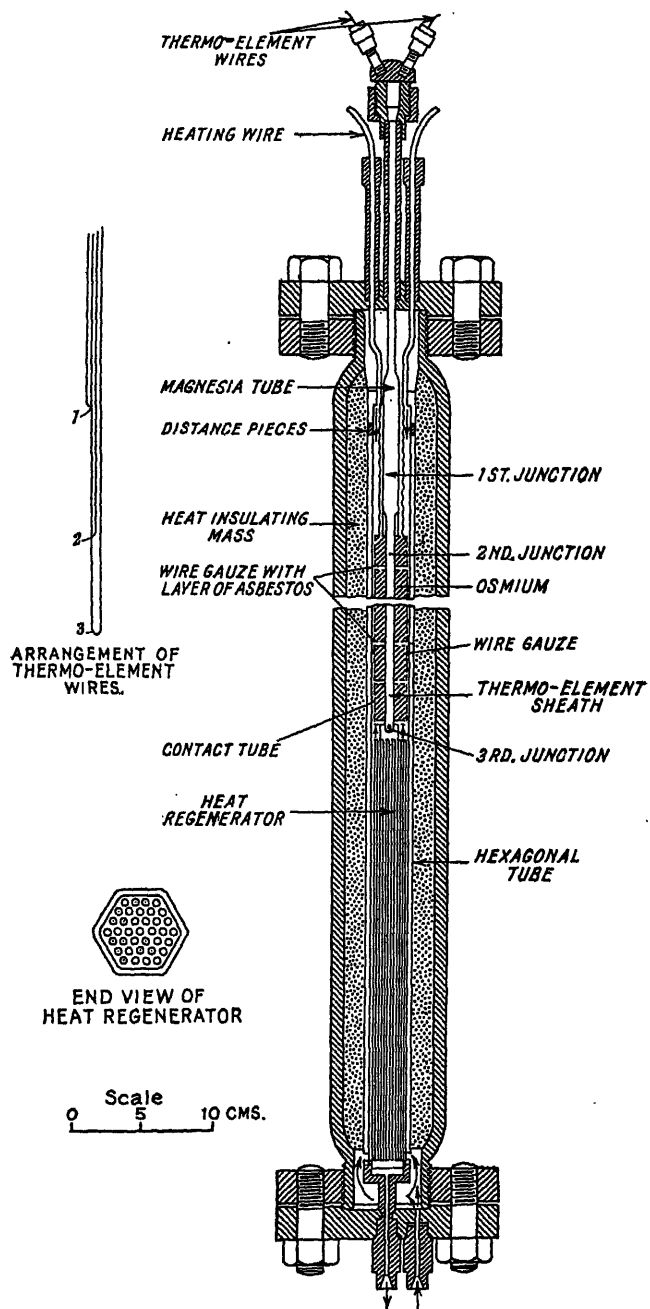


FIG. 15.

represented in Fig. 16. The multitubular heat exchanger, and the catalyst tube, both made of thin steel not intended to withstand pressure, were enclosed in a strong alloy steel pressure-resisting shell, thickly lagged on the inside. The remainder of the apparatus consisted of a circulating pump (1), which drove the high pressure gases first through a cold interchanger (2), where they were cooled, to refrigerated coils (3), where Ammonia liquefied and collected in a receiver (4). The gases then passed back through the cold interchanger (2), where they absorbed heat, to a drier (5), and the furnace (6), when the circulation commenced afresh. Original heating

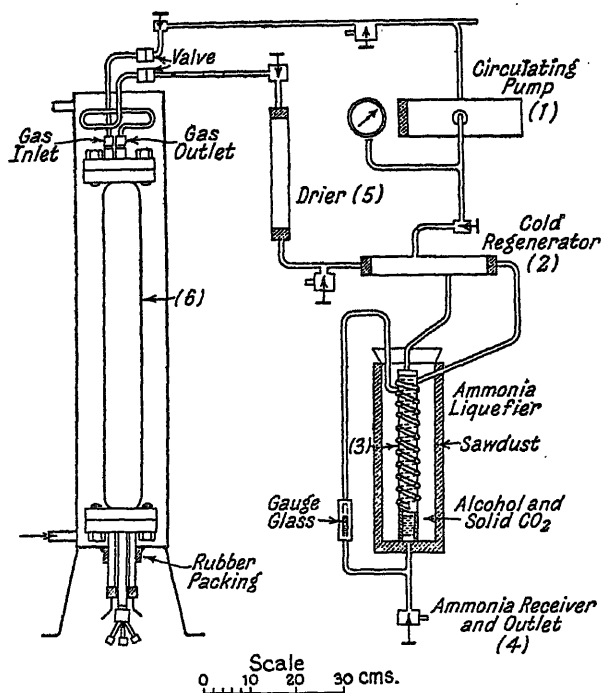


FIG. 16.

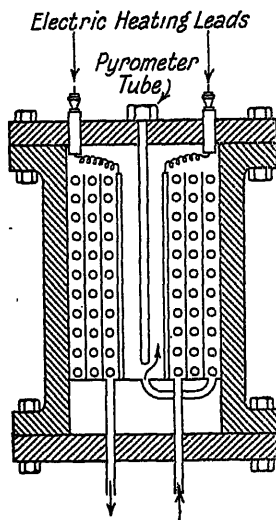


FIG. 17.

of the catalyst to start the reaction, and additional heat required to maintain it, was supplied electrically by a resistance coil wound round the catalyst tube.

A later, and more compact form, in which more perfect heat interchange occurs in a coil embedded in heat-insulating material and surrounding the catalyst tube, is shown in Fig. 17 (Rideal and Taylor, "Catalysis in Theory and Practice"). The thin steel shell containing the catalyst is electrically heated to start the reaction, which, when proceeding normally, is almost sustained by the heat of reaction, the inpassing gases reaching 550°C. by heat exchange in the coils.

Furnaces which have more recently been constructed are very large, and more complicated in internal design, aiming at greater heat conservation by better exchange and relatively lower radiation. Thus, at the Oppau works of the Badische Company, the catalyst bombs consist of alloy (probably Tungsten) steel tubes, 12 metres long, in two flanged 6-metre sections bolted together, the internal diameter being 80 cm. and the metal 18 cm. thick. Fitting internally is a pure Iron liner, $\frac{1}{2}$ inch thick, which protects the outer casing from the action of hot compressed reducing gases (see E.P. 1490 of 1912; U.S.P. 1188530 of 1916, and D.R.-PP. 254571 and 256296 of 1911). This liner makes gas-tight joints with the end caps which close the tube, and are held by fifteen 4-inch studs. The outer casing is perforated with small tapering holes so that gases penetrating the liner, owing to its permeability at a high temperature, cannot set up pressure between the liner and outer casing. The further internal construction of the furnace is secret, but there are two other iron sheaths, fitting loosely within, which are concerned with heat regeneration, or initial heating of the catalyst, also a refractory heat-insulating material, and a tube of about 50 cm. diameter for the catalyst. This operates at about 600° C., while the outer casing, which is heavily lagged on the outside, does not rise above 300–400° C.

The heat interchangers consist of tubes (steel forgings) of about 6 metres length and 38 cm. internal diameter, fitted internally with tube plates carrying 2 cm. tubes autogenously welded. The bomb and its heat interchanger are mounted vertically in a brickwork compartment with a little of the bomb projecting. The daily output per unit amounts to 20 tons of anhydrous Ammonia. Preliminary heating of the catalyst is effected by addition of Oxygen, which, however, must not come into contact with the catalyst. It is presumed that the annular sheathings are concerned in this operation. Electrical means of supplying heat are also available (D.R.-P. 359870 of 1911; U.S.P. 1202995 of 1916; see also Partington, *J. Soc. Chem. Ind.*, 1921, 40, 99).

In the United States a design of converter has been developed by the Fixed Nitrogen Research Laboratory comprising the following points (*J. Ind. Eng. Chem.*, 1925, 17, 775). The outer pressure-resisting shell, of Chrome-Vanadium steel (composition already stated), forms the outer wall of an annular space through which the cold compressed gases entering the furnace first pass. These gases are then heated by contact with nests of coils which conduct the gases from the catalyst. The catalyst is disposed along three annular spaces, an arrangement which smooths out the temperature gradient, since the first space, where the speed of gaseous interaction is greatest, is narrow, and the rate of flow correspondingly fast. The second space

is wider, and the flow therefore slower, while the third space is widest of the three. The temperature of the catalyst is recorded by pyrometer junctions, and provision is made for internal electrical heating.

The Italian process, developed by Luigi Casale, differs from the other modifications of the Haber process mainly in the much greater pressure—up to 500 atmospheres—that is employed. At this pressure,

much greater conversion per passage is obtained, with the result that the temperature of the catalyst can be sustained by the heat of reaction with much less efficient heat interchange, while the separation of the Ammonia formed is easily accomplished by liquefaction (*Chem. and Met. Eng.*, 1924, 30, 198).

The most recent type of furnace, shown in Fig. 18 (U.S.Ps. 1408987 of 1922, 1478549 and 1478550 of 1923), consists of a strong flanged pressure tube (1) closed by caps (2 and 3) at the ends. These caps hold in place two plugs (9 and 10) which support a series of tubes to form a heat interchanger. The Nitrogen and Hydrogen mixture first passes via a passage (30) to the annular space (13), of which the outer casing forms the internal wall. It then traverses the second annular space (14) upwards, and reaches the chamber (18) containing the electrical heating element, through a passage (32) in the upper plug. The heated gases then pass through the catalyst

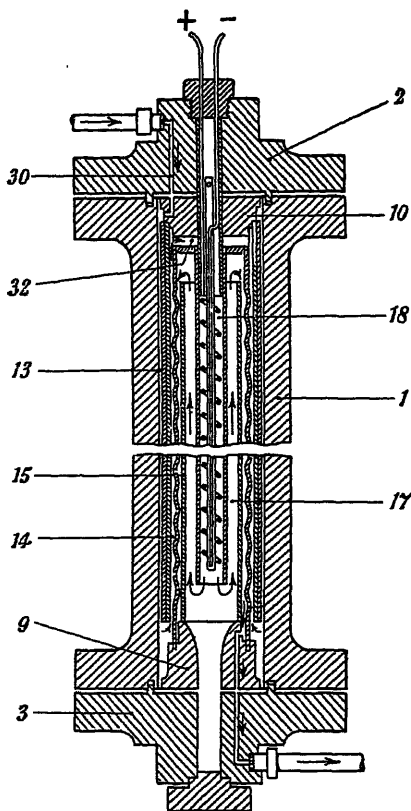


FIG. 18.

chamber (17), and out by way of an annular space (15), where heat is exchanged to the incoming gases. By interposing a heat interchanger between the external walls and the source of heat, which is at the centre of the tube, the pressure-resisting parts of the apparatus are exposed only to the temperature of the incoming gases, which is less than 400° C., and well below the point at which compressed Hydrogen has any action upon steel.

The Claude Process

The variation of the original Ammonia process due to Georges Claude has been described in a number of papers by Claude himself

in the *Comptes rendus* and other French scientific publications, and in a very large number of patents taken out by Claude and the Société L'Air Liquide in all the important manufacturing countries of the world (*C.R.*, 1919, 169, 649, 1039; 1920, 170, 174; 1921, 172, 442; 173, 653; 1922, 174, 157, 681; 1923, 176, 394; *Bull. Soc. chim.*, 1920, 27, 705; *Chemical Age*, 1920, 3, 56; *Chimie et Industrie*, 1920, 4, 5; *Science et Industrie*, 1921, 82; *Industrie Chimique*, 1921, 8, 455; Meyer, *Z. angew. Chem.*, 1923, 36, 404, and English Ps. 130086, 130087, 142150 of 1918; 140082, 140083, 140089, 155302, 156135 of 1920; 158849, 160811, 161195, 171970, 171972, 174041 of 1921; 177494, 177777 of 1922).

The process is characterised by the use of "superpressures," reaching 1000 atmospheres, or about 7 tons per square inch. From this, a number of considerable advantages follow. Thus, the equilibrium mixture at 1000 atmospheres and 550° C. contains 41 per cent. of Ammonia, as against 13 per cent. at the pressure (200 atmospheres) used in the Haber process. Much higher conversions are therefore obtained at each contact of the gases with the catalyst, as much as 40-42 per cent. being usual, corresponding with a percentage of Ammonia in the gases after contact of about 25 per cent. as compared with 5 to 7 per cent. in the Haber, while the relative productions of Ammonia per hour per litre of catalyst space are about 6000 grams and 350 grams, respectively. On account of the higher conversion, autothermic working becomes easier to attain, in fact, it would appear from recent patents that a regulated withdrawal of heat from the catalyst must be arranged when working at such high pressures. The much increased conversion also renders possible a very satisfactory separation of the Ammonia formed by simple liquefaction, while the very high pressures are also economical in regard to power. Thus, the energy required for compression varies directly as the logarithm of the pressure; that is, to raise a certain mass of gas from pressure P_1 to P_2 requires an amount of energy

$$= \log \frac{P_2}{P_1} \times \text{constant.}$$

Since $\log 1000 = 3$, and $\log 100 = 2$, the energy required to raise a certain quantity of gas from 1 atmosphere to 100 atmospheres is twice as great as the additional amount required in further raising the pressure to 1000 atmospheres. Hence the energy required for compression diminishes as the pressures become greater. The possible conversion of Nitrogen and Hydrogen into Ammonia, on the other hand, increases in direct proportion to the pressure.

The size of the apparatus in the Claude system, both on account of the greater compactness to which the reactants are brought and

the greater conversion, is much less for a given output than in the case of systems operating at a lower pressure. Thus, the size of a Haber unit, producing 20 tons of anhydrous Ammonia per day, has already been shown. Its weight is over 70 tons, and the time required for changing a catalyst, and restarting an operation is at least three days. Such a size is necessary to economise heat, loss by radiation being in this way reduced to a minimum, enabling the reaction to be sustained autothermically by an efficient heat interchange. Claude furnaces, necessary to secure the same output, weigh only 11 tons, and the external heat interchange need not be so thorough. The smaller size of plant enables gas tightness to be more easily secured, an advantage especially evident in the case of connecting tubes (8-millimetre bore suffices for plant producing 5 tons of Ammonia per day)—making both for strength and ease of joining.

Materials suitable for construction of Claude reaction vessels have been the subject of much research (see especially, Guillet, *Chimie et Industrie*, 1923, 9, 109). Nichromes (Nickel-Chromium alloys) have been used extensively, also steels containing up to 18 per cent. of Tungsten or 13 per cent. of Chromium, which retain their properties fairly well up to 600° C. More recently, an alloy referred to as "A.T.G." in French P. 496929, manufactured by the Aciéries d'Imphy, has been used, and is stated to combine in a very high degree the necessary qualities of strength and resistance to action of reducing gases at a high temperature (Claude and Soc. L'Air Liquide, E.P. 155302 of 1920). The properties of "Vichronic" and other steels since manufactured by Messrs. Vickers, of Sheffield, are said to be even more remarkable.

The pressure-resisting shell of the catalyst vessel is bored out from solid cast metal, and consists of a tube, 7 feet long, about 9½ inches external diameter, and 4 inches bore. The catalyst tube proper is made of Iron, and is attached to the plug which closes the pressure tube, being secured by an interrupted thread exactly like the breach mechanism of a heavy gun, gas-tight jointing being obtained by seating upon a Copper washer. Each of these complete tubes weighs about 14 cwt., and the head, containing the catalyst, can be changed conveniently in 10 minutes.

In the Claude system, owing to the much greater conversion, mechanical circulation of the gases over the catalyst is unnecessary, equally good results being obtained by three or four contacts only, and these are provided for by a number of catalyst tubes in series, the Ammonia produced in each being removed by cooling before arriving at the next. Actually, Claude recommends four catalyst tubes per set, the gases passing "in parallel" through the first two and "in series" through the two last. Fig. 19 is a diagrammatic representation.

Nitrogen and Hydrogen from the storage reservoirs are drawn first through flowmeters (1), which enable their rates and proportions to be adjusted, to the valve (2), where they are mixed. At the compressor (3), the mixture is raised to 100 atmospheres pressure, and after passing a water and oil separator (not shown) is raised to 900–1000 atmospheres by the supercompressor (5). Another oil and water separator (6) follows, from which the gases pass *via* the heat interchanger (7) to the protector furnace (8). This is constructed in exactly the same way as the converter furnaces, and contains as catalyst the activated Iron that has been used in the converters

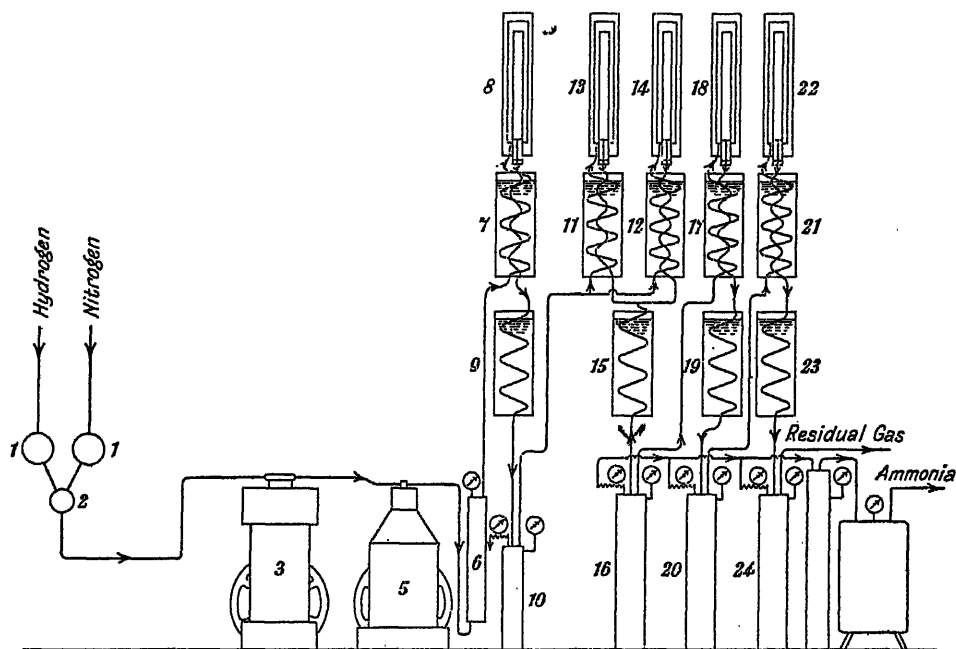


FIG. 19.

until it has become insufficiently active for Ammonia synthesis. This is kept at about 400°C ., at which temperature the Iron completely hydrogenates Carbon monoxide to Methane and water, and removes all Oxygen by combustion. After repassing the heat interchanger (7), the gases pass to the cooler (9), where water condenses and collects in the receiver (10). The purified gases then pass through the heat interchangers (11) and (12), and the first two converter furnaces (13) and (14) in parallel, returning through the heat interchangers (11) and (12) to the cooler (15), where the Ammonia formed is liquefied and caught in the receiver (16). The uncombined gases then continue through the heat interchanger (17), catalyst furnace (18), back through the heat interchanger (17) to

the cooler (19) and receiver (20), and repeat the series of operations a third time through the heat interchanger (21), catalyst furnace (22), cooler (23), and receiver (24). The exhaust gases, consisting of uncombined Nitrogen and Hydrogen, amounting to about 20 per cent. of that used, are then returned to the process.

In the catalyst furnaces, the reaction starts and stops suddenly. Thus, at a certain temperature the reaction at once commences vigorously, and continues as long as the catalyst is hot enough and active. Lastly, when the temperature has fallen too low, or the catalyst has become inert at the particular working temperature, the action stops equally abruptly. Initial heating of the reaction vessels is effected electrically, which, on account of their moderate size, is quite practicable. When the gases are passed, at the working pressure of the process, the difficulty then is to dissipate the heat sufficiently rapidly.

Calculation shows that with four tubes disposed as shown, if a is the proportion of gases combining at each contact, the percentage conversion to Ammonia of the whole set will be

$$100a(3 - 3a + a^2).$$

In practice, a 40 per cent. conversion per contact, yielding a gas mixture containing 25 per cent. of Ammonia, is obtained. Substituting $a = 0.4$ in the above expression gives a value of 78 per cent. for the conversion of Nitrogen and Hydrogen by passage through the apparatus, agreeing with the conversions actually obtained in practical working. The output from a set of four catalyst tubes of the size described, and arranged as indicated, is 5 tons of anhydrous Ammonia per day.

In conclusion, it may be noted that experience of working at high pressures has shown that a "burst" of the apparatus (as distinct from an explosion) is always in the nature of a rend, or split, and unaccompanied by any flying fragments.

CHAPTER X

DEHYDROGENATION

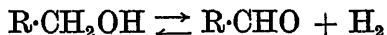
Introduction. Knoevenagel's Researches. The Equilibrium between Hydrogenation and Dehydrogenation. Dehydrogenation of Hydrocarbons and simple Derivatives. The Cracking of Oils. Manufacture of Hydrogen by Decomposition of Organic Substances. Dehydrogenation of Alcohols. Manufacture of Formaldehyde. Preparation of Acetaldehyde. Dehydrogenation of Amines. Dehydrogenation of Schiff's Bases. Degradation of Aromatic Amines and Alkyl Anilines. Dehydrogenation between Benzene and Ammonia. Fusion of Aromatic Nuclei by Dehydrogenation.

SABATIER's conception of hydrogenation, that it depended upon the formation of a labile intermediate union between the catalysing metal and Hydrogen, led him to investigate whether this affinity between metal and Hydrogen would induce the reverse change, dehydrogenation. Apparent instances of this action had been observed as early as 1823, when Dulong and Thénard showed that Iron, Copper, Silver, Gold, Platinum, etc., catalysed the decomposition ("dehydrogenation") of Ammonia (*Ann. Chim. Phys.*, 1823, (2), 23, 440).

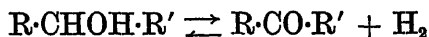
Reiset and Millon noticed that Alcohol vapour, though stable when passed through a tube containing fragments of porcelain at 300° C., lost Hydrogen even at 220° C. when the tube contained Platinum-black (*Ann. Chim. Phys.*, 1843, (3), 8, 280).

The action of Iron in facilitating decomposition of Acetylene was noticed by Berthelot (*C.R.*, 1866, 62, 906), and the similar action of Platinum-black by Schützenberger ("Traité de Chimie," 1, 724). These reactions were investigated in greater detail by Moissan and Moureu, and by Sabatier and Senderens in reactions we have already described.

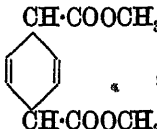
The first systematic study of the catalytic effects of metals on organic compounds was undertaken by Knoevenagel and co-workers, while almost simultaneously the catalytic dehydrogenation of alcohols to aldehydes was discovered by Ipatiev, and developed by Sabatier and Senderens, who showed that, using a Copper catalyst, the changes



and

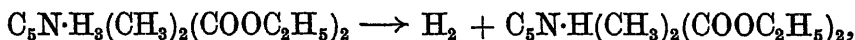


proceeded almost quantitatively between certain limits of temperature.

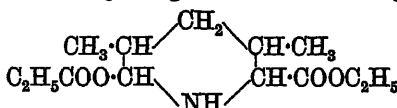
Knoevenagel and Bergdolt showed that when $\Delta^{2:5}$ -Dihydro-terephthalic methyl ester, , was heated with spongy

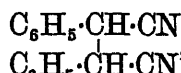
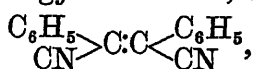

Platinum, it was completely changed, but that instead of the theoretical evolution of 113 c.c. of Hydrogen per gram of ester, only 1.4 c.c. were obtained at 140° C. and 18 c.c. at 230° C. Examination of the product showed that dehydrogenation to Terephthalic ester had been accompanied by hydrogenation to the hexahydro-ester, which was isolated in both cis- and trans-forms (*Ber.*, 1903, 36, 2857).

Knoevenagel and Fuchs showed that 3:5-Dimethyl dihydropyridine 2:6-dicarboxylic ethyl ester (2 grams) heated with spongy Palladium (0.1 gram) behaved similarly. The volume of Hydrogen liberated increased as the temperature was raised, finally corresponding almost exactly with theoretical dehydrogenation to Dimethyl pyridine dicarboxylic ester,



the rate of reaction following closely the monomolecular law. At lower temperatures, however, less Hydrogen was evolved, part being consumed in hydrogenation, forming Dimethyl piperidine

dicarboxylic ester,  (*Ber.*, 1903, 36, 2848).

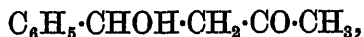
Diphenyl succinonitrile, , was found by Knoevenagel and Bergdolt to lose simultaneously Hydrogen (H_2) and Hydrocyanic acid (HCN), when heated to 180° C. with spongy Palladium, being converted respectively into Dicyanostilbene, , and Phenyl cinnamitrile, . The Hydrogen set free

in the former case was not, however, liberated as such, but consumed in hydrogenating part of the Diphenyl succinonitrile or Dicyanostilbene to Benzyl cyanide. The change was nearly quantitative, since 10 grams of dinitrile gave 3.5 grams of Benzyl cyanide, 2 grams of Dicyanostilbene, 3 grams of α -Phenyl cinnamitrile, and 0.38 gram of Hydrocyanic acid (*Ber.*, 1903, 36, 2861).

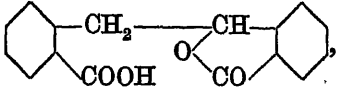
Dehydrogenation may be truly regarded as the reverse action

of hydrogenation, and many instances of equilibrium, especially between aldehydes, ketones, and alcohols, in which the rate of hydrogenation is balanced by the rate of dehydrogenation, have been recorded by Ipatiev and others. In general, the equilibrium is favourable to hydrogenation at a low temperature, dehydrogenation becoming more pronounced as the temperature is raised, while increase of pressure, as would be expected from Le Chatelier's rule, is favourable for hydrogenation. Thus, Ipatiev showed that the decomposition in presence of Iron of primary, secondary, or tertiary alcohols, either by dehydrogenation or dehydration, was diminished by increased pressure, and though the course of reaction when it occurred was the same as at ordinary pressure, yet the products formed were obtained in different proportions, due to the various possible reactions taking place in different relative degrees (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 786; *Ber.*, 1904, **37**, 2961). These conclusions were reached as a result of experiments on Methyl, Ethyl, Propyl, isoPropyl, and Amyl alcohols, Acetaldehyde, Acetone, and Dimethyl ethyl carbinol.

These considerations explain why Copper can function either as a dehydrogenating or hydrogenating catalyst. On account of its weak activity, relatively to Nickel, a higher temperature is often necessary before it exerts any action, in which case dehydrogenation becomes the predominating change. For example, alcohols in contact with Copper are not attacked below 230° C., at which temperatures (at ordinary pressures of Hydrogen) dehydrogenation takes place. Kubota and Hayashi have found, however, that by increasing the pressure of Hydrogen and lowering the temperature ketones are converted into secondary alcohols (*Bull. Chem. Soc. Japan*, 1926, **1**, 14). The ketones were heated in presence of Copper powder in an autoclave, with Hydrogen at 60 to 90 atmospheres. Acetophenone, under these conditions, at 140° C. gave Phenyl methyl carbinol, and at 160° C. Ethyl benzene. Benzophenone, $(C_6H_5)_2CO$, at 120° C. gave Diphenyl carbinol, $(C_6H_5)_2CHOH$, and Diphenyl methane, $(C_6H_5)_2CH_2$, and at 190° C. Diphenyl methane and Tetraphenyl ethane, $(C_6H_5)_2CH \cdot CH(C_6H_5)_2$. Camphor at 120–150° C. gave Borneol and isoBorneol, while from Benzil at 100° C. Benzoin (43 per cent.), Hydrobenzoin and isoHydrobenzoin were formed: the latter two becoming the main products (Hydrobenzoin 74 per cent. and isoHydrobenzoin 14 per cent.) when the temperature was raised to 130° C. Benzoyl acetone, $C_6H_5 \cdot CO \cdot CH_2 \cdot CO \cdot CH_3$, at 83° C., while mostly unchanged, gave some of the keto alcohol,



and at 105° C. was reduced more completely to the glycol, $C_6H_5 \cdot CHOH \cdot CH_2 \cdot CHOH \cdot CH_3$. Phthalic anhydride at 120° C. formed

70 per cent. of the reduction product, , together with 12 per cent. of Dihydroxyphthalan, $C_6H_4 \begin{matrix} \text{CHOH} \\ \text{CHOH} \end{matrix} O$.

That the equilibrium is by no means complete in the sense of complete hydrogenation even at the ordinary temperature has been shown by Wieland, who effected some small degree of dehydrogenation by shaking solutions of various substances with Palladium-black carefully freed from Oxygen. These experiments also indicated the probability that the same point of equilibrium would be reached whether the initial materials were the saturated substances, or the dehydrogenated product plus Hydrogen. By shaking with Palladium-black, aqueous Hydroquinone gave some Benzoquinone and Quinhydrone; Hydrazobenzene in Benzene solution gave partially Azobenzene and Aniline; Dihydronaphthalene in Benzene gave Naphthalene and Tetrahydronaphthalene, and Dihydroanthracene, also in Benzene, gave Anthracene. The Hydrogen tended either to remain with the Palladium, or to be consumed in hydrogenation. It was observed that the Palladium did not function purely and simply as a catalyst, since its active mass shifted the position of equilibrium in the reaction, owing doubtless to its affinity for one of the reactants. Increasing the amount of metal moved the equilibrium in the direction of increased dehydrogenation (*Ber.*, 1912, 45, 484).

Dehydrogenation of Hydrocarbons, and Simple Derivatives

According to Sabatier, all hydrocarbons, aliphatic, alicyclic, or aromatic, in contact with a catalysing metal at a certain definite temperature commence to part with their Hydrogen, this temperature depending upon the power of the catalyst and the stability of the hydrocarbon. Simultaneously, the molecule of hydrocarbon tends to split into residues, $CH_3\cdot$, $CH_2\cdot$, and $CH\cdot$; capable of reuniting with one another to more stable configurations, or of hydrogenating and then recombining, or of decomposing completely into Carbon and Hydrogen. Above a certain temperature, this resolution proceeds to completion.

Methane is slowly attacked by catalytic Nickel at $350^\circ C.$, at $390^\circ C.$ the action is fast. Ethane slowly decomposes at $325^\circ C.$, giving free Hydrogen, Carbon and Methane. Other saturated hydrocarbons behave in a similar way; thus, Pentane at $350-400^\circ C.$ gives Methane and intermediate hydrocarbons, and Hydrogen, with deposition of Carbon on the Nickel. Generally, the more complex the carbon chain the lower the temperature at which the decom-

position commences (Sabatier and Senderens, *Ann. Chim. Phys.*, 1905, (8), 4, 435).

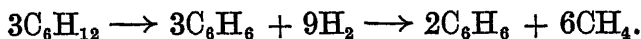
Ethylene passed over reduced Nickel at 300° C. is totally decomposed, forming a mixture of Ethane, Methane, and Hydrogen (partially used to hydrogenate Ethylene to Ethane), while a voluminous mass of Carbon soon blocks the tube. The proportions of Ethane and Methane fall as the temperature is raised, and at a red heat only small quantities of products other than Carbon and Hydrogen are obtained (Sabatier and Senderens, *C.R.*, 1897, 124, 616, 1358). Propylene undergoes a similar decomposition, and produces a mixture of Propane, Ethylene, Ethane, Methane, and Hydrogen (Sabatier and Senderens, *C.R.*, 1902, 134, 1128).

The similar but much faster decomposition of Acetylene has already been described. In contact with finely-divided Nickel containing occluded Hydrogen, Acetylene commences to react at the ordinary temperature and, being endothermic, sufficient heat is generated to raise the catalyst to incandescence. If all adsorbed Hydrogen is first removed from the Nickel, however, pure Acetylene does not commence to decompose until the Nickel has first been raised to 150–180° C. At this temperature, three independent reactions then take place simultaneously: (1) Destruction of Acetylene to Carbon and Hydrogen. (2) Condensation to Cuprene. (3) Hydrogenation by the Hydrogen formed in (1) followed by various recombinations, giving complex petroleum-like mixtures of aliphatic, aromatic, and hydrocyclic hydrocarbons. At higher temperatures, especially at incandescence, the well-known Berthelot polymerisation occurs with the portions of Acetylene escaping decomposition, whereby Benzene, Styrene, and hydrogenated Naphthalenes and Anthracenes are formed.

Other metals, especially Cobalt, Iron, and Platinum, are also dehydrogenating catalysts, and behave in all cases like Nickel, though less energetically. Copper is much more moderate, and requires a considerably higher temperature (Sabatier and Senderens, *Ann. Chim. Phys.*, 1905, (8), 4, 430).

The activity of metals for dehydrogenation is roughly in proportion to their activity as hydrogenators: thus, the hydrogenating metal catalysts have the most marked dehydrogenating influence, but dehydrogenation and degradation are actions which substances tend to undergo on exposure to a high temperature alone, and most contact substances facilitate it to some degree ("cracking"). For example, the finely-divided reduced oxides give energetic dehydrogenating preparations (see Kusnetzov, *Ber.*, 1907, 40, 2871; Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1911, 43, 1431). This dehydrogenation, general for all organic substances above a certain temperature, is in most cases complicated by far-reaching degradative changes, brought

about, as Sabatier supposed, by disruption of the molecule into residues which are capable of hydrogenation, reunion, or further decomposition. For example, Cyclohexane derivatives in contact with a dehydrogenating metal tend to revert to the corresponding aromatic body. Nickel again is the most active catalyst, and the Hydrogen liberated reacts with a portion of the original substance to give aliphatic hydrocarbons. With Cyclohexane, this action commences at about 270° C. :



The less stable Cyclohexene, C_6H_{10} , reverts more easily to Benzene, and gives a nearly quantitative yield with Nickel at 250° C. (Padoa and Fabris, *Atti R. Accad. Lincei*, 1908, 17, (1), 111, 125).

With Methyl cyclohexane, decomposition commences at 240° C., and is very rapid at 275° C., giving a mixture of Hydrogen, Methane, and Toluene. Ethyl cyclohexane similarly decomposes at 280–300° C., giving Hydrogen, Methane, Ethyl benzene, and Toluene. Reduced Copper is much less energetic but effects the same reactions at about 300° C. (Sabatier and Senderens, *C.R.*, 1901, 133, 568; Sabatier and Mailhe, *ibid.*, 1903, 137, 240).

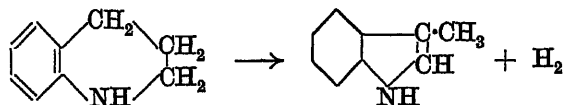
Cyclohexanol and its homologues tend to revert to the corresponding phenols in contact with Nickel, and efforts by Skita and Meyer to hydrogenate Cyclohexanone at 230° C. in presence of Nickel resulted in the formation, even in presence of excess of Hydrogen, of 25 per cent. of Phenol ("Sabatier's Reaction and its Reversal," *Ber.*, 1911, 44, 668, 968). The yield of dehydrogenated substance in most cases is, however, low, on account of degradative changes supervening.

Polyhydroxy cyclohexanes tend to lose Hydrogen more easily than Cyclohexanol, but at the same time the tendency towards elimination of hydroxy-groups is also increased, and lower phenols and Benzene are formed. Cyclohexylamine and Dicyclohexylamine similarly revert to a certain amount of Aniline and Diphenylamine, respectively. Hydrides of Naphthalene are dehydrogenated, the decahydro-body giving the tetrahydro- with Nickel at 200° C., and this regenerating Naphthalene at 300° C. In the case of hydrides of Anthracene and Phenanthrene, and, in fact, very generally, the Hydrogen liberated assists in the catalytic reduction to simple aliphatic chains. Thus, Decahydrophenanthrene with Nickel at 200° C. splits into lower hydrides and various aliphatic hydrocarbons, before undergoing complete dehydrogenation to Phenanthrene, which requires a temperature of about 280° C. Hydrogenated Anthracenes and Decahydrofluorene behave in the same way, reverting ultimately, with degradative bye-products, to Anthracene and Fluorene, respectively.

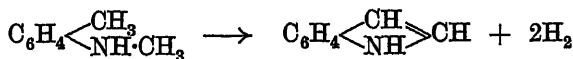
Since the laws of substitution in the Naphthalene and the Tetrahydronaphthalene series are different (*e.g.*, nitration or halogenation of Tetrahydronaphthalene gives a more or less easily separable mixture of α - and β -isomerides, while from Naphthalene almost exclusively the α -compound is obtained), the possibility exists of obtaining the more difficultly accessible β -Naphthalene derivatives by substitution in Tetrahydronaphthalene and then dehydrogenating. Braun, Hahn, and Seeman (*Ber.*, 1922, 55B, 1687) found that dehydrogenation of Tetrahydronaphthalene derivatives could be effected smoothly in an atmosphere of Carbon dioxide by passage through an empty tube at 650–680° C., or by contact with pumice and Lead oxide at the same temperature. In this way, β -Ethyl tetrahydronaphthalene and β -Tetrahydronaphthyl methyl ketone gave the corresponding Naphthalene derivatives. Tetrahydroacenaphthene and its derivatives often dehydrogenated with the same ease, giving Acenaphthene, or Acenaphthylene compounds, but Hydrindene could not be treated in the same way, since conditions sufficiently drastic to dehydrogenate this substance led to very extensive decomposition.

Ciamician claims that Piperidine is dehydrogenated completely to Pyridine with Nickel at 180–250° C. (*Atti R. Accad. Lincei*, 1907, 16, 808), whether Hydrogen is present or not—at variance with results obtained by Padoa (*ibid.*, 1907, V, 16, (1), 818), who obtained a complex mixture of products, containing but little Pyridine.

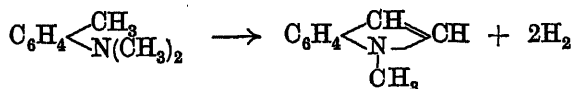
Tetrahydroquinoline at 180° C. with Nickel gives some Quinoline, but a larger proportion undergoes intramolecular rearrangement, with formation of β -Methyl indole (Skatole),



(Padoa and Scagliarini, *Atti R. Accad. Lincei*, 1908, 17, (1), 728). Padoa and Carrasco obtained a similar interesting transformation by submitting Mono- and Di-methyl orthotoluidines to dehydrogenation in presence of Nickel at 300–330° C., when a 6 per cent. yield of Indole was obtained in the former case,

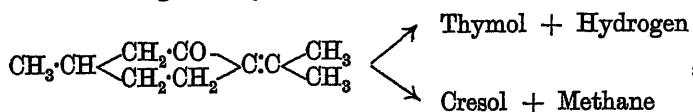


(*Atti R. Accad. Lincei*, 1906, 15, (2), 699) and a 24 per cent. yield of *n*-Methyl indole in the latter,



(*Gazz.*, 1907, 37, (2), 49).

In presence of Hydrogen, with Nickel at a high temperature, simultaneous dehydrogenation and rehydrogenation to a stabler product may occur. For example, Pinene passed with Hydrogen over Nickel at 360° C. is converted into Menthane. Limonene or Camphene by the same treatment gives a mixture of Cymene and Cumene, Menthene gives Cymene, Pulegone gives Cresol and Thymol,



while Eucalyptol, Terpene, and Terpineol undergo dehydration simultaneously with dehydrogenation, and give Cymene (Sabatier and Gaudion, *C.R.*, 1919, 168, 670).

During the war efforts were made to augment supplies of nitratable aromatic hydrocarbons by degradation of complex substances such as turpentine (see, for example, Sabatier, Mailhe, and Gaudion, *C.R.*, 1919, 168, 926). Very deep-seated changes occurred, with formation of a number of gaseous and liquid products, containing aromatic substances, as well as Carbon, which deposited on the catalytic metal and soon enfeebled its activity.

Other metals exert a dehydrogenating action: Platinum and Palladium in a superior degree, and Iron and Copper in an inferior. The actions of the two former metals have been investigated by Zelinsky and co-workers, who showed that Palladium was the more powerful agent, and with Cyclohexane derivatives induced considerable reaction even at 170° C. and rapid reaction at 200° C., often giving fair yields of the corresponding aromatic compounds (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1220; 1912, 44, 275; *Ber.*, 1911, 44, 2305; 1912, 45, 3677).

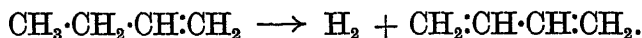
On the other hand, simple Cyclopentane derivatives and Cycloheptane were not acted upon below 300° C. Zelinsky showed that catalytic dehydrogenation by Palladium and Platinum at temperatures up to 300° C. could be applied to purification of hydrocarbons of the Cyclopentane series from Cyclohexane compounds, and to the examination of petroleum distillates. Thus, a mixture of Methyl cyclopentane and Cyclohexane vapours was passed three times over Platinum-black at 300° C. The Hydrogen produced corresponded with 93.4 per cent. of the theoretical for conversion of the Cyclohexane present into Benzene, and the product, after shaking with Sulphuric acid (containing excess of free Sulphuric anhydride) to sulphonate the aromatic bodies, gave a residual hydrocarbon which after distillation over metallic Sodium possessed the properties of pure Methyl cyclopentane.

The process of dehydrogenation of Cyclohexane hydrocarbons was extended by Zelinsky and Uklonskaja to simple derivatives, and

the results are described in the last two papers mentioned. Cyclohexane carboxylic acid added to Palladium-black at 300° C., in an atmosphere of Hydrogen at 20–25 mm. pressure, gave Benzoic acid. The ethyl ester behaved similarly; but the Methyl cyclopentane carboxylic acids, like the parent hydrocarbon, resisted dehydrogenation.

Copper as a dehydrogenating agent requires a much higher temperature to decompose hydrocarbons. Mannich resolved Dodecahydrotriphenylene into Triphenylene and Hydrogen by contact with Copper at 450–500° C. (*Ber.*, 1906, 40, 159).

Butadiene, or Erythrene, an intermediate for synthetic rubber, can be prepared catalytically, and several patents have appeared describing various methods. According to E.P. 9722 of 1911, 1:2-Butylene is passed through a tube containing red-hot metallic Copper, when dehydrogenation results in direct formation of Butadiene,



It can also be prepared by simultaneous catalytic dehydrogenation and degradation of Cyclohexane. According to E.P. 448 of 1912, the vapour is passed over a spiral of Aluminium silicate, heated electrically to a dull red heat. In either case, the unchanged hydrocarbons are recovered and returned to the process, while the Butadiene is polymerised to rubber by contact with metallic Sodium.

The Cracking of Hydrocarbons

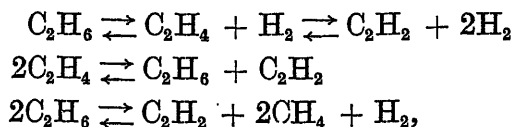
Closely related to the general subject of dehydrogenation and degradation of hydrocarbons is the technical process of obtaining from high boiling ("heavy") mineral oils a lower-boiling decomposition product, capable of replacing petrol, or petroleum ether, in most of the uses to which these substances are applied.

It was noticed by Murdock, as far back as 1792, that when a heavy oil was decomposed by heat a gas of high illuminating power was produced. The simultaneous formation of other products, low boiling oils, aromatic hydrocarbons, and volatile fuels—suitable for driving internal combustion engines—has also been known for a long time.

The first patent was taken out by Atwood, in 1860 (U.S.P. 28246), in which a method was described of obtaining a high yield of illuminating substances, this consisting simply in the distillation of high boiling oils at atmospheric pressure. The application of pressure to raise the boiling point, and so increase the percentage of oil decomposing during distillation, was first suggested by Young in 1865 (E.P. 3345), and independently by Benton in 1866 (U.S.P. 342564). These processes did not, however, aim at a complete distillation and condensation under pressure—a result first achieved in the Dewar-Redwood process (U.S.Ps. 419931 and 426173 of 1890).

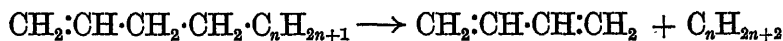
At the time these processes were proposed, they possessed no technical interest, since kerosene was a more valuable product than gasoline. The reversal of this order was directly due to the development of the motor industry—commencing about the turn of the century—and more recently to the introduction of power-driven aircraft, by which time the original patents had expired, or were forgotten. Other factors have also contributed to increase the demand for low-boiling oils—notably the great European war, and an interdependent factor, the rapid progress of industrial chemical processes. As a consequence, the demand for the low-boiling fractions of natural petroleum became so great that no outlet could be found for the large quantities of high-boiling constituents produced at the same time, and the conversion of the latter into the former became a necessary balancing factor in the economics of the oil-refining industry. Accordingly, and especially in the oil-producing districts of America, the “cracking” of heavy mineral oils, as this process is called, has attained enormous importance, producing artificially large quantities of petrols and paraffins, as well as Benzene and Toluene, for use as solvents, illuminants, and fuel for internal combustion engines, or for general purposes in chemical industry. The rate of progress and its coincidence with the rise of the motor industry are shown by the following facts. The first process for the production of light fuels from heavy oils was established on a technical scale by Burton in 1912. In 1923, the total output of the United States of light oils for the motor industry amounted to 7556 million gallons, of which no less than 2000 million gallons were produced by cracking the heavier fractions.

Generally the cracking process is carried out by simple application of heat, whereby under the combined influences of temperature and pressure the complicated hydrocarbon molecules are broken down into simpler ones. To explain this disruption, the nascent radicle theory of Sabatier and Senderens has been elaborated by Bone and Coward (*J.S.C.*, 1908, 93, 1197), according to which the radicals $\cdot\text{CH}$, $\cdot\text{CH}_2$, and $\cdot\text{CH}_3$ (and more complicated ones) set free by the decomposing hydrocarbon immediately recombine to simpler and stabler configurations. Berthelot, however, regarded the process as essentially one of dehydrogenation, leading to the formation of an olefinic (or polyolefinic) hydrocarbon, together with (in most cases) Methane. For example, the following sequence of reactions was suggested in the case of Ethane,



the primary products remaining, or undergoing further decomposition to simpler substances, or Carbon and Hydrogen, according to their stability under the conditions employed (*C.R.*, 1866, 62, 905; 63, 788; *Bull. Soc. chim.*, 1867, II, 7, 251). The presence of olefines and polyolefines in cracked oils is easily demonstrated, but acetylenic compounds, as postulated by Berthelot, have not been found. This does not, however, show that they are not formed, since under the conditions of working their decomposition or polymerisation to aromatic bodies would be expected.

The formation of polyolefinic hydrocarbons, which occur in considerable quantities in crude cracked oils, may be due to the elimination of further equivalents of Hydrogen, or, as Ostromisslenski has suggested, to decomposition of mono-olefines, with scission of a saturated hydrocarbon, as follows :



(*J. Russ. Phys. Chem. Soc.*, 1910, 42, 145; 1915, 47, 194).

The physico-chemical theory of the cracking processes has been examined by Rittman (*J. Ind. Eng. Chem.*, 1915, 1916, and 1917, several papers).

It was shown by Berthelot and by Ostromisslenski that the pyrogenous decompositions of oils were much influenced by the presence of catalysts. The temperature of decomposition is much lowered by almost any contact body, and the course, both of the initial decomposition and of the subsequent synthetic processes, may be much modified.

The first definite proposal to effect the resolution of high boiling oils by catalytic means was due to Sabatier, in 1908 (see F.P. 400141 of 1909). By passing the vapour of heavy oils over finely-divided metals, such as Iron, at a dull red heat, a light spirit was obtained, together with Hydrogen and other gaseous products. By fractionally distilling the product, and repeating the process with the higher boiling fraction, it was shown that oils could be completely resolved into low boiling or gaseous products, and Carbon, which remained on the catalyst, but which could be removed as water gas by passing steam at a high temperature. The liquids obtained in this way were largely unsaturated compounds, and possessed a disagreeable odour, removed by hydrogenation in presence of Nickel at 150–300° C.

Removal of polyolefinic hydrocarbons from light oils intended for use as motor spirit is desirable, since these substances tend on standing—especially in light—to polymerise to gummy, non-volatile substances, which choke or otherwise hinder the action of the engine valves. Mono-olefines, or paraffin hydrocarbons, do not in general undergo this polymerisation, and their presence is admissible. Poly-

olefinic hydrocarbons can also be removed by fractional extraction with small quantities of strong Sulphuric acid.

In a modification of his earlier patent, Sabatier proposed to pass the vapours of the heavy oil over a network of electrically heated wires at 500° C. to red heat, or over a catalyst at about 300° C., consisting of finely-divided metals or oxides, such as Iron oxide. Alternatively, salts capable of easy reduction to metal, mixed with a neutral refractory material free from Silica, such as Magnesia, Alumina, or graphite, were suggested, together with an agglutinant (glue, dextrin, or starch) which must also be free from Silica (F.P. 475303). The unsaturated hydrocarbons produced were then hydrogenated as before.

Since Sabatier's original patent for the catalytic cracking of oils, many others have appeared, employing the catalyst to effect the decomposition either in the liquid or vapour phase. Most of the stable metals, in a finely-divided or a coarse form, as well as their oxides and other compounds, and all the commoner refractories have been proposed, more especially the following: Iron, Nickel, Cobalt, Silver, Chromium, Copper, Manganese, the Platinum metals, alloys, or oxides of these metals, firebrick, natural silicates, and ores (Bauxite, etc.). These substances have generally been employed for vapour-phase cracking, in which case the presence of steam has often been claimed an advantage (Examples: E.Ps. 13675 of 1908, 28460 of 1911, 20074, 20075, 25631, 25832 of 1912; F.P. 451471 of 1912; E.Ps. 16611, 17121, 24491 of 1913; 4573 of 1914, etc.).

The manner in which it was proposed to work these processes was as follows: According to the earlier Hall patents (*e.g.* E.P. 17121 of 1913), hydrocarbon vapours were heated to 600° C., or higher, under a pressure of 5 atmospheres, in presence of a metallic or an oxide catalyst (Nickel, Iron, etc.) capable of fixing Hydrogen, then allowed to expand when the Carbon was deposited, and finally condensed. According to E.P. 5434 of 1914, mineral oils, or their residues, may be heated to 400–650° C. in the liquid state with quick lime, or a mixture of quick lime and Carbon. The procedure of E.P. 11420 of 1914 consists in passing vaporised oil, together with steam, over Iron oxide, or the oxide of some other metal capable of several states of oxidation, at 500–600° C. Catalysts used in this way become quickly choked with Carbon and need frequent regeneration by heating in air.

Active catalysts for the conversion of heavy oils can be made by heating powdered metallic oxides, or mixtures of oxides, with organic salts of the same metals. For example, a mixture of Ferric oxide, Nickel oxide, and Carbon with Ferrous oxalate and Nickel oxalate can be incorporated with tar, and briquetted and sintered in a closed crucible. Other very effective metals are Chromium, Cobalt, or

Manganese, while small amounts of Alumina, Ceria, Magnesia, or other oxides of the "earth" group are stated to promote the action (E.P. 5847 of 1914). The presence of Alumina or Titania considerably increases the proportion of aromatic substances formed.

A certain proportion of Benzene is formed when petroleum and Hydrogen are heated to 180–300° C. in the presence of certain catalysts, such as Aluminium, Iron, Cobalt, Nickel, Copper, Silver, Zinc, or Platinum, or alloys, or mixtures of oxides of these metals.

The presence of Ammonia in vapours to be cracked is stated to reduce considerably the separation of Carbon on the catalyst, and also to enable a light spirit free from Sulphur to be obtained, even from a heavy oil containing a large proportion, such as Mexican, in which the proportion may be as high as 5–6 per cent. The catalyst is prepared by heating a metallic oxide, or mixture of oxides, with an organic compound, *e.g.*, an oxalate or a tartate of the metal. The vaporised oil is first partially decomposed by contact with the catalyst, and the product received by fractionators and condensers. Part of the uncondensed gases then passes through an Ammonia saturator under slight pressure, and thence to the still, where, impinging upon the surface of the oil, the process of distillation is considerably facilitated (E.Ps. 17272, 20470 of 1913; 2838 of 1914).

These processes did not, however, attain any practical significance. In large scale practice, vapour-phase cracking was found to involve serious difficulties, chiefly connected with deposition of Carbon, which were most easily overcome by working in the liquid phase. This also enabled a simpler and more compact plant to be employed, and gave a greater rate of output. Accordingly, vapour phase operation, and the use of catalysts, came to be almost entirely abandoned, except in some few instances where an Iron catalyst has been adopted.

Of a different type of catalytic decomposition are those processes in which an anhydrous inorganic chloride, especially Aluminium or Ferric chloride, is heated with the liquid oil. This is added to the oil in any form of still, and since it induces decomposition below the boiling point of many heavy oils, application of pressure is unnecessary. Processes operating with Aluminium chloride have been patented by Gray (E.Ps. 17838 and 17839 of 1913); McAfee (E.P. 22243 of 1914; U.S.P. 1127465 of 1915), and Athel (E.Ps. 7112, 17838 of 1913); and have obtained considerable favour. Since pressure distillation is unnecessary, except in the case of unusually volatile oils, the apparatus can be simple and safe, involving no risks other than the normal ones attending simple distillation of inflammable liquids. Moreover, the yields are good, and the product is of exceptional quality. These advantages over the non-catalytic pressure processes are, however, more than offset by the cost of the Aluminium chloride,

which is difficult to recover in anhydrous form from the oil residues. The mode of operation has been described in detail by McAfee, the originator of the process (*J. Ind. Eng. Chem.*, 1915, 7, 737).

Water and light fractions are first distilled from the oil to be treated, which is then placed in a simple closed still provided with a stirrer and connected with condensers. It is then heated to 260–290° C. with a suitable proportion of anhydrous Aluminium chloride. Decomposition products soon commence to distil, together with a certain amount of volatilised Aluminium chloride. The vapours first pass to two air-cooled condensers in series, where a high and a lower boiling fraction are separated. The high fraction, together with the Aluminium chloride, which condenses with it, are returned to the still, while the vapours which pass both air-cooled condensers are conducted (at about 175° C.) to a water-cooled condenser. The light oil here obtained is nearly colourless and sweet smelling, and consists of a mixture of gasoline, solvent oil, and kerosene. It is stated to be nearly saturated, requiring therefore no treatment with strong Sulphuric acid, the only purification necessary being a washing with dilute aqueous alkali to remove a small amount of Sulphuretted hydrogen. After a time, the Aluminium chloride becomes inert, being embedded in a mass of coke. It can be recovered by sublimation at a red heat in a current of Chlorine, or, after removing the bulk of the oil, by extraction with water. In this case, a strong aqueous solution is obtained, hydrolysing to Alumina on concentrating, which is reconverted into the anhydrous chloride by heating with Carbon in a current of dry Hydrochloric acid. The yields of gasoline obtained from Cuddo and Oklahoma oils are 43.3 and 34.8 per cent., respectively, as against 18 and 12.5 per cent. when the ordinary liquid phase processes are employed.

The high cost of anhydrous Aluminium chloride has militated against McAfee's process, while the numerous difficulties encountered in vapour-phase cracking, with or without a catalyst, have led to the supersession also of such methods in favour of cracking in the liquid phase. This was first carried out on a technical scale by Burton, for the Standard Oil Company of Indiana, U.S.A., in 1912 (basic patent, U.S.P. 1049667 of 1913). Many variations of the Burton process have since been patented, and a large number are in technical operation. All possess a fundamental principle in common, that the oil is decomposed by heating in the liquid state to 400–700° C., this being carried out in a simple pressure vessel, and the low boiling products so formed being then isolated by fractionation. In modern practice, it has become usual to arrange a continuous distillation, raising the boiling point to the point of decomposition by allowing a suitable pressure to develop within the apparatus.

The original Burton stills consisted of large cylindrical vessels,

constructed of $\frac{1}{2}$ - to $\frac{7}{8}$ -inch mild steel plate, riveted and calked, leak-tight jointing being eventually obtained by Carbon deposition. These were charged with oil and heated to about 375° C., when cracking commenced, and the pressure was allowed to rise to 5 to 6 atmospheres by the gases evolved. Distillation was continued for 48 hours, by which time the temperature rose to 450° C., and a distillate collected amounting to some 60 per cent. of the oil originally charged. The residue in the still, containing granular Carbon in suspension, was then charged into retorts and distilled to coke, which amounted to about 5 per cent. of the oil charged into the coking still, while the distillate from this still was then used in the cracking still. On rectification, the yield of gasoline per charge usually amounted (with a suitable quality oil) to 30–35 per cent., with a degree of unsaturation not greater than about 10 per cent. The gases evolved consisted chiefly of Methane, Ethane, Ethylene, and Hydrogen.

The most serious difficulties encountered in this process were due to deposition of Carbon, which accumulated in safety and run-off valves, and was also liable to crust on the bottom of the still, rendering heating under pressure dangerous. Hence in the earlier types of still, distillation for 48 hours was often impossible. Humphreys' modification consisted in inserting movable plates in the still in such a way that deposition of Carbon tended to occur on the plates, when distillation could be carried much farther in each operation.

Many later modifications, named after their originators, such as the "Cross," "Fleming," "Dubbs," etc., processes, arrange a circulation of oil, first through a preheater, then through tubes suitably protected, and heated in a furnace to the cracking temperature. From the tubes, the oil is immediately discharged into a capacious vessel, the reaction vessel, heavily lagged to economise heat, when the conversion into lighter oils and the deposition of Carbon occur, accompanied with a slight fall of temperature. No external heat is applied to the reaction chamber. The converted oil is then allowed to escape from the reaction chamber through a valve, manipulation of which enables the pressure in the whole system to be controlled. Up to 30 per cent. of gasoline may be present in this oil, which is obtained by simple distillation, and the remainder returned to the cracking still.

Such types of plant possess many advantages over the original still-cracking method. In the first place, in the newer forms of plant only a small proportion of the oil undergoing treatment is in the heated zone at any one moment, with correspondingly lessened risk of fire. Carbon is not deposited in the furnace tubes, through which the oil circulates rapidly, but in the capacious reaction

chambers, which are not externally heated, and which, being large, can be run a long time before becoming overcharged with Carbon. Often several large reaction chambers are attached to each cracking unit.

The working temperatures and pressures vary for the different processes. In the Cross system, the oil is preheated to 175°C . and raised in the furnace tubes to $450\text{--}500^{\circ}\text{C}$. while a pressure of 40 atmospheres prevents vaporisation, and the cracked oil containing its gasoline is discharged from the reaction chamber.

The nature and composition of the products depend very greatly upon the temperatures and pressures employed. Generally the lower the temperature of working the less dehydrogenation occurs and the lower is the proportion of unsaturated and cyclic hydrocarbons formed. Hence, the Burton and the Fleming processes give a product with a comparatively low content of unsaturated bodies, consisting mostly of hydrocarbons of the paraffin series, while it is one of the disadvantages of the vapour-phase processes that they yield the highest proportion of unsaturated compounds. It may be noted, however, that recent patents describe various catalytic methods whereby these unsaturated oils can be easily polymerised to lubricating oils of high viscosity.

At higher temperatures— 700°C . upwards—the proportion of unsaturated and aromatic bodies increases; while as the pressures increase there is a tendency towards increasing molecular complexity of the compounds obtained. Several systems—notably the Rittman—have been specially devised to yield the maximum of aromatic constituents (especially Toluene) with the gasoline.

The system best adapted to the large scale, which gives the maximum latitude in regard to pressure, temperature, and other conditions of working, is the Dubbs process. The oil is pumped to the furnace coils, part directly, and part by way of the dephlegmator, where it is preheated by condensing cracked vapour. A large number of coils, consisting of tubes about 40 feet long and 4 inches diameter, form the heating unit, the oil flowing through these from below upwards and passing thence directly to the reaction chamber. This is a large cylindrical vessel, capable of holding 30–35 tons of coke, and heavily lagged. Here the cracking is completed without the necessity of any additional heat. The vapours from this chamber pass to the dephlegmator, and are separated as desired into high- and low-boiling fractions, a conduit being arranged to convey the former back to the furnace coils, while the latter pass on to condensers. The liquid residuum in the reaction vessel is continuously drawn off, while the coke remains.

The temperature of the vapour leaving the dephlegmator, that is, the boiling point of the gasoline formed and the amount of oil

refluxing back for recracking, depends on the temperature at which the dephlegmator is maintained by the charging oil which is used to cool it. Hence the nature of the product can be controlled within wide limits by adjusting the proportions in which the oil is charged directly, or *via* the dephlegmator, to the furnace coils.

The light vapours, after condensation, are caught in a pressure distillate receiver, whence the liquid is gradually released along with the necessary amount of gas to maintain a steady pressure, as desired (generally about 9–12 ats.) in the system.

The length of the runs depends upon the time taken for the reaction chamber to become overcharged with coke. Sometimes several chambers are installed for each cracking unit, in which case the process becomes almost completely continuous, since in a well-designed plant deposition in the heating tubes should be very small. By variation of the temperature, pressure, rate of cracking, and the temperature of the dephlegmator, it is claimed that a Dubbs unit will resolve oil into practically only gasoline and coke, or into various proportions, as desired, of gasoline, gas oil, fuel oil, and coke.

References to the literature of the cracking of oils have been collected by Lomax, Dunstan, and Thole (*J. Inst. Pet. Tech.*, 1916, 3, 9, 36–120). Since the date of this paper, general descriptions of cracking processes have been given by Brookes, Bacon, Padgett, and Humphrey (*J. Ind. Eng. Chem.*, 1915, 7, 180), and by Brownlee (*Chem. and Met. Eng.*, 1924, 31, 737, 812, 848). The Hall process has been described in *Engineering*, 1915, 99, 250, and in *J. Gas. Lighting*, 1915, 129, 455; the Cross process in *Oil and Gas News*, February, 1924, and the Dubbs process by Morrell, in *Chem. and Met. Eng.*, 1924, 31, 1006.

Mailhe has shown that fats or oils (glycerides or fatty acids) of animal or vegetable origin can be decomposed by the ordinary cracking methods and yield a mixture of products not unlike those obtained from hydrocarbon oils (*Ann. Chim.*, 1922, IX, 17, 304). Linseed oil (*C.R.*, 1921, 173, 358), Rape oil, Oleic acid (*C.R.*, 1922, 174, 873), Shark oil (*Bull. Soc. chim.*, 1922, IV, 31, 249), and Arachis oil (*ibid.*, 1922, IV, 31, 567) were decomposed by passage of their vapours over a catalyst at 550–650° C., for which purpose electrolytic Copper, Magnesia, but chiefly a Copper–Aluminium alloy were used. The liquid products formed were then hydrogenated in contact with finely-divided Nickel, when in each case a complicated mixture was obtained in which aliphatic, aromatic, and cyclic hydrocarbons, especially Benzene, Toluene, Xylene, Cyclohexane, and Methyl cyclohexanes, were identified, and, in some cases, many of the higher fatty acids. Gaseous products also were formed freely, containing olefines and paraffins, Carbon monoxide and dioxide.

Manufacture of Hydrogen by Decomposition of Organic Substances

Beyond a certain temperature, the decomposition of hydrocarbons and of organic bodies proceeds to completion, that is, resolution occurs to completely stable products, such as Carbon, Hydrogen, water, and oxides of Carbon. In the case of the stabler hydrocarbons, such as members of the paraffin series, especially Methane, a very high temperature is necessary—above 900°C .—before the rate of decomposition into Carbon and Hydrogen becomes rapid. Presence of contact catalysts in such cases is an advantage, enabling decomposition to be effected at a much lower temperature.

The first patent for the manufacture of Hydrogen by decomposition of hydrocarbons was taken out by St. John (E.P. 1466 of 1876), who showed that it could be obtained freely by passing coal gas over red-hot coke. Shortly after, Stern passed naphtha vapour with steam over heated lime (E.P. 2787 of 1880). These two patents are typical of many that subsequently appeared. Of those which have been applied technically, the most important are the Carbonium Gesellschaft, the Rincker and Wolter, the Cechelhauser, and the Bunte (B.A.M.A.-G.) processes.

The Carbonium Gesellschaft process applies the Machtolf patent (E.P. 14601 of 1906), in which Acetylene, mixed with oil gas, at a pressure of 4 to 6 atmospheres, is exploded electrically. The products are Hydrogen and lampblack, both in a very pure form, the technical success of the process depending largely upon the value of the latter product, which is very finely divided, and must be separated from the Hydrogen by filtration. Several other patents describing safe methods for the decomposition of Acetylene have since appeared.

Pictet has suggested using the heat of decomposition of Acetylene ($\text{C}_2\text{H}_2 \rightarrow 2\text{C} + \text{H}_2 + 47,800 \text{ cal.}$) as a source of heat for decomposing another substance mixed with it. Thus, according to E.P. 24256 of 1910, Acetylene, alone or mixed with another hydrocarbon, is decomposed in a chamber maintained at about 500°C . by the heat of decomposition of the Acetylene.

Other patents by Pictet protect the decomposition of oils, such as petroleum, by heat alone, such as passage of the vapour through a tube at $1200\text{--}1350^{\circ}\text{C}$. (E.P. 13397 of 1911). Addition of steam is claimed an advantage in E.P. 14703 of 1911, while in E.P. 16373 of 1911 it is proposed to maintain the decomposition temperature by admission of oxygen or air to effect combustion of a portion of the petroleum passing.

In the Bunte and the Cechelhauser processes, coal gas is passed over heated coke. In the former the Carbon monoxide is removed from the coal gas before treatment, and a Hydrogen results which is said to contain the Nitrogen of the coal gas as the only important

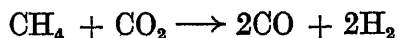
impurity. The latter process simply passes coal gas over coke at 1200° C. and filters the lampblack from the product, which consists of 80–84 per cent. Hydrogen. A similar use of coal gas has been proposed by Lessing (E.P. 15071 of 1909).

In the Rincker and Wolter process, generators resembling those used for making water gas are filled with coke, and heated by passage of a blast of air. Alternating with these blasting periods, tar, oil, or other hydrocarbon bodies are sprayed in or otherwise introduced, and decomposed into Hydrogen and Carbon, the latter being deposited within the generator (F.Ps. 391867, 391868 of 1908). Many other patents apply this principle. A modification of the process evaporates oil in a chamber heated by the waste gases from a generator during the heating phase and passes the vapour so formed over the red hot coke in another generator. In this way, the deposition of difficultly combustible Carbon is avoided (E.P. 2054 of 1914).

Brownlee and Uhlinger suggested carrying out the decomposition in a chamber filled with refractory material, alternately heating it by combustion of fuel gases, and employing the heat stored to decompose hydrocarbons. The lampblack formed was partly carried away by the Hydrogen and recovered by filtration or deposition (E.P. 5098 of 1915, U.S.P. 1363488).

Herman arranged to burn natural gas (mostly Methane) with the calculated quantity of air to give Nitrogen and Carbon dioxide, utilising the heat liberated to split up more Methane into Carbon and Hydrogen. Both the combustion and the decomposition were carried out under pressure, when the water and Carbon dioxide were easily separated by liquefaction. At 950° C. the decomposition of Methane was stated to be complete, and at lower temperatures only partial (D.R.-P. 303881).

The assistance of catalysts has been proposed in a large number of patents. Dieffenbach and Moldenhauer passed a heated mixture of oil and steam through gauze of some catalytic metal, such as Nickel or Platinum (D.R.-P. 229406 of 1909). Nauss suggested the decomposition of coal gas by contact with Nickel at 250–300° C. (E.P. 2298 of 1910). The Badische Company also have decomposed oil and steam by contact with a catalyst consisting of 2 to 5 per cent. of Nickel on a Magnesia support, maintained at 800–1000° C. (E.P. 12978 of 1913). According to a later patent of this company (D.R.-P. 306301, addition to 296866), when hydrocarbons and steam are passed over Nickel, the reaction



takes place to an extent increasing as the temperature rises.

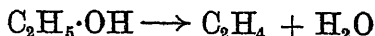
Prins obtained Hydrogen by mixing Carbon, or a carbo-hydrogenous body with a suitable solid catalyst, passing steam over the

mixture at 300–600° C., and removing Carbon dioxide from the product. The catalysts mentioned were salts of the alkali or alkaline-earth metals, such as Calcium phosphate (E.P. 128273 of 1917).

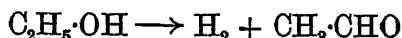
Dehydrogenation of Alcohols

It was first observed by Berthelot and Jungfleisch that when Ethyl alcohol is passed through a heated tube, it commences to decompose at about 500° C., the decomposition consisting of two distinct superposed reactions:—

1. Dehydration to Ethylene and water



2. Dehydrogenation to Acetaldehyde



("Traité de Chimie Organique," Paris, 1886).

In contact with various catalytic agents it is now known that dehydration may take a third course, or, rather, stop at an intermediate stage, giving Ether.

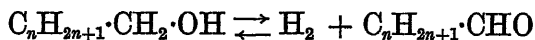
3. $2\text{C}_2\text{H}_5\cdot\text{OH} \longrightarrow (\text{C}_2\text{H}_5)_2\text{O} + \text{H}_2\text{O}.$

Ipatiev showed that the proportion in which alcohol undergoes these three changes is very much modified by the presence of catalysts: that is, different catalysts increase the speeds of the three reactions by widely different factors, and Sabatier has drawn up a table in which the relative dehydrating and dehydrogenating influences of various oxides are compared. At the one extreme, oxides like Alumina and Thoria are almost exclusively dehydrating. At the opposite extreme, other oxides and metals, such as Zinc or Manganese oxides, and metallic Nickel or Copper, are almost exclusively dehydrogenating, while other substances occupying an intermediate position accelerate to varying degrees both reactions simultaneously. In the present chapter we are concerned solely with dehydrogenation. Sabatier's table will be considered in connection with "Dehydration."

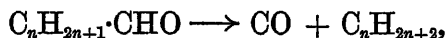
The dehydrogenation of alcohols was first studied by Ipatiev, who obtained the corresponding aldehydes or ketones by treatment of Methyl, Ethyl, isoButyl, isoAmyl, Benzyl, and isoPropyl alcohols with the following catalysts at a suitable temperature: a Platinum tube, Zinc rods (the form of the Zinc much affected the relative proportions of dehydrogenation or dehydration products respectively, since Zinc dust gave from Ethyl alcohol mainly Ethylene, which partially decomposed into Carbon and Hydrogen), Brass containing 33 per cent. of Zinc, Iron, Graphite, and Aluminium. The decomposition of the aldehyde formed to Carbon monoxide and paraffin hydrocarbon was also observed. Allyl alcohol gave Acrolein, which,

however, under the conditions of its formation, largely underwent further change (*Ber.*, 1901, 34, 3579; 1902, 35, 1047; *J. pr. Chem.*, 1903, ii, 67, 420).

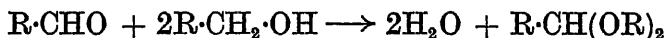
It is to Sabatier and Senderens that we owe a complete understanding of the dehydrogenation of alcohols. They showed that when primary saturated alcohols are passed over finely-divided Copper the action



commences at about 200° C., becomes rapid at 250° C., and is almost the exclusive reaction up to 300° C., or even higher, hence providing an excellent general method of preparing aldehydes. At higher temperatures, the aldehydes commence to decompose into Carbon monoxide and a hydrocarbon,

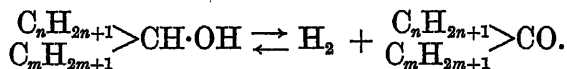


and at 400° C. this decomposition is usually almost complete. Reduced Nickel acts similarly, but more energetically and at a lower temperature. It has, however, the disadvantage of inducing decomposition of the aldehyde to Carbon monoxide and hydrocarbon at all temperatures at which dehydrogenation is possible, while a further bye-reaction, the decomposition of Carbon monoxide to Carbon and Carbon dioxide, which sets in at a higher temperature, may cause carbonisation of the catalyst. Cobalt reacts like Nickel, while spongy Platinum requires a higher temperature than Copper, and therefore brings about greater destruction. Small quantities of acetals are often formed by dehydration between aldehyde and unchanged alcohol,



(Sabatier and Senderens, *C.R.*, 1903, 136, 921).

Secondary alcohols are dehydrogenated more easily than the primary, and since ketones are usually stabler substances than aldehydes, the reaction is even less susceptible to complications,



The conversion either of primary alcohols into aldehydes or of secondary alcohols into ketones can never be complete, since the reactions are reversible, but the yields (allowing for recovered alcohol) are in most cases very good. By working at reduced pressure, more complete hydrogenation is attainable, since by reducing the "active mass" of the Hydrogen formed the reverse action is retarded. This procedure is of considerable advantage also when using alcohols of low volatility (*Bouveault, Bull. Soc. chim.*, 1908, (4), 3, 50, 119).

Tertiary alcohols are unable to undergo dehydrogenation, so that the alternative reaction, dehydration, is effected instead. At 280–400° C., finely-divided metals rapidly resolve tertiary alcohols into water and olefinic hydrocarbon (Sabatier and Senderens, *C.R.*, 1903, 136, 983).

According to the action of catalytic Copper at 300° C., Sabatier and Senderens proposed a method of distinguishing experimentally between primary, secondary, and tertiary alcohols; aldehyde, ketone, or olefinic hydrocarbon being formed respectively (*Bull. Soc. chim.*, 1905, iii, 33, 263).

Ethyl alcohol vapour in contact with reduced Copper commences to lose Hydrogen at 200° C., and is rapidly dehydrogenated at 250° C., giving Acetaldehyde. Up to 300° C., this reaction occurs almost without complication. At 420° C., however, the gaseous products of the reaction contain also Methane and Carbon monoxide in equal proportions, formed by decomposition of Acetaldehyde,



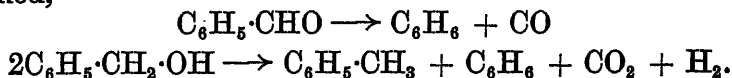
a reaction which, in presence of Copper, commences about 400° C. Using Nickel, Ethyl alcohol commences to decompose about 150° C., and decomposes rapidly at 170° C.; but decomposition of the aldehyde to Carbon monoxide and Methane occurs simultaneously to a certain degree, this decomposition becoming greater as the temperature rises, while some of the Hydrogen and Carbon monoxide interact to give excess of Methane. At 230° C., carbonisation of the Carbon monoxide commences. Cobalt gives similar results, while spongy Platinum does not commence to react until 270° C., at which point the Acetaldehyde formed is mostly decomposed into Carbon monoxide and Methane (*C.R.*, 1903, 136, 738).

Using Copper, Sabatier and Senderens also obtained the following results :—

Normal Propyl alcohol dehydrogenated smoothly to Propylaldehyde between 230° C. and 300° C. At 420° C., rapid decomposition of the aldehyde occurred. *n*-Butyl alcohol gave Butylaldehyde between 220° C. and 280° C.; which decomposed at 370° C. isoButyl alcohol, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{OH}$, at 240–300° C. easily gave isoButylaldehyde, which decomposed rapidly at 400° C. isoAmyl alcohol, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, at 240–300° C., gave the aldehyde without any side reaction, but at 370° C. the usual decomposition (Sabatier and Senderens, *Ann. Chim. Phys.*, 1905, (8), 4, 463).

Aromatic alcohols are dehydrogenated in the same way, but require a higher temperature, and the range within which satisfactory results are obtainable is relatively narrow. With Benzyl alcohol, the reaction with Copper commences about 300° C., giving

Hydrogen and Benzaldehyde smoothly, but at 380° C. by-reactions occur, and Carbon monoxide and dioxide, Benzene, and Toluene are formed,

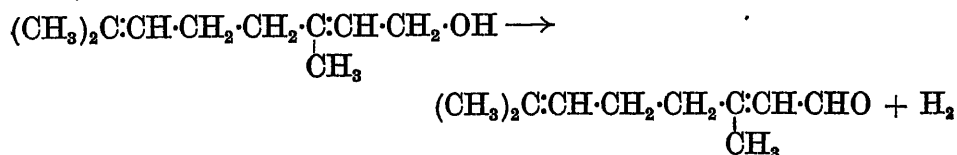


Phenyl ethyl alcohol, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, gives similarly the corresponding Phenyl acetaldehyde, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CHO}$, best under diminished pressure.

Unsaturated alcohols are dehydrogenated in a similar manner, but the Hydrogen generated is partially used in hydrogenating, more or less completely, the unsaturated aldehyde formed, so that the final product is mostly the corresponding saturated aldehyde. Thus, Allyl alcohol, $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{OH}$, at 180–300° C., gives Hydrogen and Acraldehyde, $\text{CH}_2\text{:CH}\cdot\text{CHO}$, which interact, giving largely Propylaldehyde, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CHO}$,



(Sabatier and Senderens, *C.R.*, 1903, 136, 983). Similarly, Bouveault showed that the Undecylenic alcohol, $\text{CH}_2\text{:CH}(\text{CH}_2)_8\cdot\text{CH}_2\cdot\text{OH}$, gave only the saturated Undecylaldehyde, $\text{CH}_3(\text{CH}_2)_9\cdot\text{CHO}$. Geraniol, however, at 205° C., under reduced pressure gave almost entirely the corresponding unsaturated aldehyde, Citral,



(*Bull. Soc. chim.*, 1908, (4), 3, 50, 119).

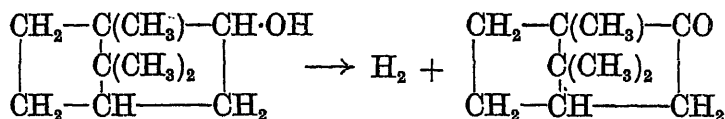
In a further investigation, Sabatier and Kubota showed that the two types of reaction, dehydrogenation and dehydration, characteristic of saturated alcohols occur in the case of Allyl alcohol. Finely-divided metals and dehydrogenating oxides, such as Manganous oxide, give almost exclusively aldehydic products. On the other hand, dehydrating oxides, such as those of Tungsten, Thorium, and Aluminium, give unsaturated hydrocarbons, while Zirconia and Urania, as before, favour both types of reaction simultaneously. Dehydration does not, however, take a smooth course, since secondary reactions always lead to more or less production of Propylaldehyde, Propylene, Acraldehyde, etc. (*C.R.*, 1921, 173, 17, 212).

A number of secondary alcohols examined by Sabatier and Senderens all gave the corresponding ketone in high yield, and nearly pure Hydrogen. isoPropyl alcohol slowly gave Acetone at 150° C., and rapidly and smoothly at all temperatures between 250° C. and

430° C., without any formation of Propylene. isoButyl alcohol from 160–300° C. similarly gave ketone and Hydrogen only. Methyl hexyl carbinol at 250–300° C. gave Methyl hexyl ketone, but at 400° C. slight decomposition into Carbon monoxide, Methane, and Hexane occurred (*C.R.*, 1903, 136, 983).

Cyclohexanol in the same way at 300° C. gave a good yield of Cyclohexanone (Sabatier and Senderens, *Ann. Chim. Phys.*, 1905, (8), 4, 467). Homologues of Cyclohexanol, viz., the three monomethyl and several dimethyl derivatives, reacted in the same way, but in some cases dehydration to the Cyclohexene derivatives and further dehydrogenation to the phenol occurred noticeably. For example, ortho-Methyl cyclohexanol gave small quantities of both ortho-Methyl cyclohexene and ortho-Cresol (Sabatier and Mailhe, *C.R.*, 1905, 140, 350; *Ann. Chim. Phys.*, 1907, (8), 10, 550).

Borneol, with Copper at 300° C., is transformed easily and nearly completely into Camphor,



(Goldsmith, E.P. 17573 of 1906; Aloy and Brustier, *Bull. Soc. chim.*, 1911. (4), 9, 763).

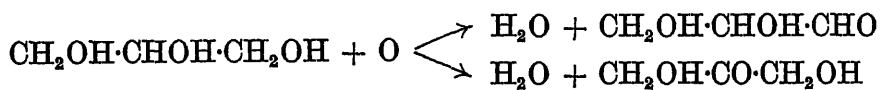
By contact with finely-divided Copper at 220–250° C., Bouveault and Locquin have dehydrogenated keto-alcohols of the type $\text{R} \cdot \text{CHOH} \cdot \text{CO} \cdot \text{R}$ to the corresponding α -diketones, $\text{R} \cdot \text{CO} \cdot \text{CO} \cdot \text{R}$, and esters of β -oxy-acids of the type $\text{R} \cdot \text{CHOH} \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$ to the keto-esters $\text{R} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$ (*C.R.*, 1905, 140, 1699; *Bull. Soc. chim.*, 1906, (3), 650). In this way, the following compounds were made from the corresponding "Acyloins" and oxy-esters: Dibutyryl, $\text{C}_3\text{H}_7 \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_3\text{H}_7$; Di-isobutyryl, $(\text{CH}_3)_2\text{CH} \cdot \text{CO} \cdot \text{CO} \cdot \text{CH}(\text{CH}_3)_2$; Di-caproyl, $\text{C}_5\text{H}_{11} \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_5\text{H}_{11}$; Dihexoyl, $\text{C}_6\text{H}_{13} \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_6\text{H}_{13}$; and isoValeryl-acetic ethyl ester, $(\text{CH}_3)_2\text{CH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$. This method furnishes one of the best general methods for the preparation of the symmetrical diketones, since the preparation of the "acyloins," or keto-alcohols, by condensation of esters in presence of metallic sodium has been completely investigated by Bouveault in a series of papers just prior to the ones quoted, and the dehydrogenation of these bodies takes place in good yields.

The dehydrogenation of Benzhydrol, $(\text{C}_6\text{H}_5)_2\text{CHOH}$, was studied by Knoevenagel and Heckel (*Ber.*, 1903, 36, 2816, 2823). When heated alone or in an atmosphere of Carbon dioxide, Benzhydrol is transformed into Hydrogen and Benzophenone, but very slowly and incompletely even at 300° C. The presence of spongy Palladium facilitates this reaction, which proceeds monomolecularly—with forma-

tion more completely of Benzophenone with advancing temperature, up to 300° C. In presence of Copper powder, however, Benzhydrol ether, $(C_6H_5)_2CH \cdot O \cdot CH(C_6H_5)_2$, formed by dehydration, is the main product, with subsidiary amounts of Tetraphenyl ethane, $(C_6H_5)_2CH \cdot CH(C_6H_5)_2$, and Diphenyl methane, the proportion of Benzophenone being very small. Heated in complete absence of air at 210–220° C. with half its weight of Copper powder, a 70 per cent. yield of the ether may be obtained; a result which, according to Sabatier, is unique, being the only case of dehydration known under such conditions among all the catalytic actions of Copper.

The dehydrogenation process is retarded and always prevented from reaching completion by the reverse reaction. This can be minimised, and in some cases yields of aldehyde much increased by admission of Oxygen or air with the alcohol vapour to combine with the Hydrogen set free, as has long been the established principle in the manufacture of Formaldehyde by dehydrogenation of Methyl alcohol. Trillat, however, in his experiments on the oxidation of alcohols, obtained good yields of aldehyde only in the case of Methyl alcohol, by mixing air with the vapour, and subjecting to the action of a catalytic metal, the yield of aldehyde progressively diminishing as the complexity of the alcohol increased. Thus, from Ethyl alcohol and air, a 16.8 per cent. yield of Acetaldehyde was obtained, with 2.3 per cent. of the Acetal; Propyl alcohol gave similar yields, while Butyl and isoButyl alcohols gave respectively 12 and 5 per cent., and isoPropyl alcohol a 16 per cent. yield of Acetone. The tertiary alcohol, Trimethyl carbinol, decomposed into Formaldehyde, Acetone, and water. In the same way, Allyl alcohol gave 5.8 per cent. of Acrolein with a little Acrylic acid, Formaldehyde, and Glyoxal; Benzyl alcohol gave 4.0 per cent. of Benzaldehyde; Cumyl alcohol, 5.7 per cent. of Cuminaldehyde; Cinnamyl alcohol a low yield of Cinnamaldehyde, and isoEugenol a 2.9 per cent. yield of Vanillin (*Bull. Soc. chim.*, 1902, (3), 27, 797; 1903, (3), 29, 35).

Grimaux passed Glycerine vapour with air over Platinum-black, when a vigorous reaction took place, and the products contained, besides Acrolein and Formaldehyde, a certain amount of Glyceric aldehyde and Dihydroxyacetone, formed by dehydrogenation of the primary and secondary alcohol groups, respectively,

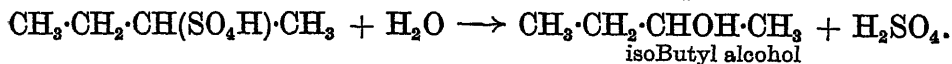
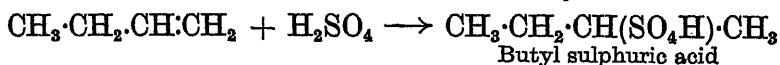
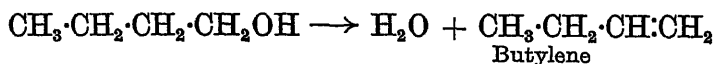


(*Bull. Soc. chim.*, 1886, 45, 481).

Much more satisfactory results have been obtained by Orlov (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 203), and more recently by Moureau and Mignonac, who have shown that under certain con-

ditions it is a considerable advantage to dehydrogenate in presence of a carefully controlled proportion of air. The latter investigators passed the vapours of various alcohols, mixed with less than the theoretical proportion of air, over a silver catalyst, mounted upon asbestos, prepared by reduction of Silver nitrate with Formaldehyde, and maintained at 230–300° C. Since the action was powerfully exothermic, it was in most cases found preferable to use even this limited supply of air in several stages, passing the vapour more than once over the catalyst. Yields varying between 60 and 96 per cent. of theory were obtained from Methyl, Ethyl, Butyl, isoAmyl, Allyl, Benzyl, Cinnamyl, isoPropyl, and secondary Butyl alcohols, and those cases in which the lower yields were obtained were markedly improved by use of diminished pressure (*C.R.*, 1920, 170, 258; 171, 652).

During the war, the production of Methyl ethyl ketone, $\text{CH}_3\cdot\text{CO}\cdot\text{C}_2\text{H}_5$, was investigated by Moureau and Mignonac (*Bull. Soc. chim.*, 1921, (4), 29, 88). In presence of strong Sulphuric acid, normal Butyl alcohol isomerises to isoButyl alcohol, presumably by way of the following series of changes:—



Sabatier and Senderens' general method of dehydrogenation with finely-divided Copper gives, with isoButyl alcohol, a very satisfactory yield of Methyl ethyl ketone, so long as the alcohol is pure. Impurities, however, quickly cause poisoning of the catalyst—an inconvenience which Moureau and Mignonac found could be readily obviated by dehydrogenation in presence of air.

Secondary Caprylic alcohol at 330–340° C., and Dodecylic alcohol at 310–320° C., both under 30 mm. mercury pressure, also gave high yields of the corresponding ketone and aldehyde, respectively, and Geraniol, treated with 30 to 40 per cent. of the theoretically requisite proportion of air under 25–30 mm. and at a temperature of 300–310° C., gave Citral without any sign of bye-reaction or decomposition.

Manufacture of Formaldehyde

Formaldehyde owed its earliest application as a disinfecting agent for rooms to its easy volatility and considerable bactericidal action. For use in this way, Methyl alcohol was originally burnt in specially constructed lamps, when, although by far the greater quantity was completely oxidised to Carbon dioxide and water, a

small proportion was converted into Formaldehyde. Various patterns of lamps were devised by Krell, Tollens, Barthel, Robinson, Schering, Trillat, Broché, Dieudonné, and others, but they have long since ceased to be used, and Formaldehyde for disinfection purposes is now dispersed by other means, such as devices for vaporising Paraformaldehyde, $(\text{HCHO})_n$, chemical oxidation of Methyl alcohol, or spraying of solutions of Formaldehyde.

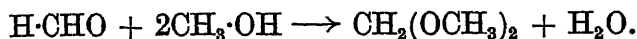
A number of other uses for Formaldehyde, both in the arts and industry, have since arisen, such as the hardening of gelatin, the preservation of food (now prohibited by reason of the toxicity of Formaldehyde), the disinfection and tanning of hides, many synthetic uses in the dyestuffs and fine chemical industries, and synthetic tannins and resins of the type of "Bakelite," formed by condensation between Formaldehyde and Phenols. In addition, processes in the brewing, distilling, sugar, paper, and textile industries use considerable quantities, while the fixing of glues and sizes and the waterproofing of fabrics by rendering gelatin or casein insoluble are among the minor applications.

For many years the only available large-scale method of manufacture of Formaldehyde has been the partial combustion (or dehydrogenation) of Methyl alcohol, and although it recently appeared that the partial combustion of Methane, as being more economical, would replace the older process, the advantages in favour of Methyl alcohol as the initial material have been completely restored by the modern synthetic method of manufacture of this substance.

Formaldehyde was discovered by Hofmann in 1867, who observed its formation during the flameless combustion of Methyl alcohol—such as may most conveniently be shown by placing a heated Platinum wire in a vessel containing Methyl alcohol vapour and air, when the wire will commence to glow and remain red hot as long as Methyl alcohol vapour and air remain. Hofmann obtained small quantities of Formaldehyde by passing the vapour of Methyl alcohol with air through a heated Platinum tube (*Ber.*, 1878, 11, 1685). Armand Gautier heated a glass tube in a Sulphur bath, and Tollens (*Ber.*, 1882, 15, 1629; 1883, 16, 917; 1886, 19, 2134), Loew (*J. pr. Chem.*, 1886, 33, (2), 324), and Kablukov also substituted a glass tube containing various catalytic materials such as Platinum or Copper foil or gauze, etc. (see also *Ber.*, 1881, 14, 2134). The yield of Formaldehyde was shown to depend much upon the air-alcohol ratio and the catalyst temperature, and addition of water to the Methyl alcohol was recommended.

The first Formaldehyde plant was designed by Trillat in 1889. Methyl alcohol was vaporised, mixed with air, and passed over Platinised asbestos at a low red heat ("Oxidation des Alcohols," 1901; F.P. 199919; D.R.-P. 55176; *Bull. Soc. chim.*, 1902, (3), 27,

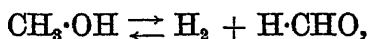
797; 1903, (3), 29, 35). Trillat soon found that a wide selection of catalysts was almost equally suitable, especially oxidised Copper, while even broken porcelain and firebrick gave good results. Often a small proportion of the Formaldehyde was condensed to Formal by reaction with unchanged Methyl alcohol,



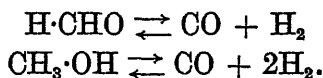
Using a Platinum gauze catalyst, a temperature near 200° C. gave the best results, further elevation of temperature much increasing the decomposition to oxides of Carbon and Hydrogen, while the presence of about 20 per cent. of steam in the Methyl alcohol vapour was also stated to be an advantage, a point contested by later workers.

By using an oxidised Copper gauze catalyst at 330° C. and passing over it a mixture of Methyl alcohol vapour and air in the proportions of 3.75 litres of the latter per gram of the former, Trillat obtained a yield of Formaldehyde of 48.5 per cent. of the theoretical. Much higher temperatures, about 500° C., are now used with faster space velocities, enabling a much greater rate of production and a rather higher yield to be obtained.

The Researches of Sabatier. Sabatier and Mailhe first directed attention to Berthelot's experiments on the heat decomposition of primary alcohols, in which it was shown that in the absence of air two simultaneous actions, dehydration and dehydrogenation, occur. They then proceeded to investigate the influence of various catalysts, metals, and oxides, on these reactions. The general results of this work have already been stated. Copper at 200–300° C. was the most effective, and when freshly prepared brought about the reaction



enabling a 50 per cent. conversion to be obtained, with a small loss only by decomposition, 45 per cent. of the Methyl alcohol being recoverable by distillation. It was found, however, that Copper below 300° C. rapidly lost its efficiency in the case of Methyl alcohol, while elevation of temperature was an unsatisfactory remedy, since at 300° C. the secondary decomposition of aldehyde into Carbon monoxide became marked, and at 350° C. rapid. Both reactions are now known to be reversible,



Sabatier selected Methyl alcohol as the most convenient alcohol to use in comparing the dehydrogenating activities of various catalysts, since the dehydration to olefine is impossible, and many catalysts which exert a mixed action, dehydrating and dehydrogen-

ating, on higher alcohols, are, at 350° C., dehydrogenating only in the case of Methyl alcohol. Using the following oxides under comparable conditions at a temperature of 350° C., the volume of Hydrogen in c.c. liberated per minute was measured as follows:—

With some oxides, the action was simple, no secondary decomposition of Formaldehyde occurring, and almost pure Hydrogen was produced.

| Oxide. | Hydrogen. | C.c. per minute. |
|--------------------------------|--------------|------------------|
| GlO | Very little. | |
| SiO ₂ | | 0.3 |
| TiO ₂ | | 1.2 |
| ZnO | | 1.5 |
| ZrO ₂ | | 1.8 |
| MnO | | 2.0 |
| Al ₂ O ₃ | | 6.0 |

Many oxides simultaneously effected a partial decomposition of the Formaldehyde produced, giving Carbon monoxide and Hydrogen, thus,

| | |
|--------------------------------|-----|
| PbO | 45 |
| Mo ₂ O ₃ | 54 |
| CdO | 57, |

while in some cases the Formaldehyde was almost completely destroyed, and the gaseous products consisted of Carbon monoxide and Hydrogen in the proportions approximately of 1 : 2 :—

| | |
|--------------------------------|-----|
| Fe ₂ O ₃ | 106 |
| V ₂ O ₃ | 140 |
| SnO | 160 |
| Copper | 152 |

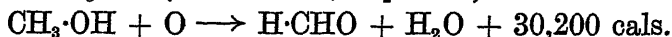
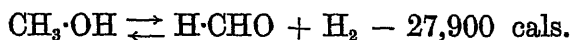
At higher temperatures, all the catalysts facilitated the more extensive decomposition.

The action of Zinc dust and Zinc oxide in decomposing Methyl alcohol into a mixture of Carbon monoxide (30 per cent.) and Hydrogen (70 per cent.) had been already observed by Jahn (*Ber.*, 1880, 13, 983). These facts guided Patart to success in his efforts to effect the reverse action, the synthesis of Methyl alcohol from Carbon monoxide and Hydrogen.

Sabatier also compared the dehydrogenating action of finely-divided metal catalysts on Methyl alcohol. Nickel commenced to dehydrogenate at 180° C., but even at this point two-thirds of the Formaldehyde decomposed to Carbon monoxide and Hydrogen, which then gave secondary gaseous products. The action of Nickel was very rapid at 250° C., but then 90 per cent. of the Formaldehyde

was destroyed. At 350° C. there was no aldehyde and no Carbon monoxide, the latter having been converted into Methane and Carbon dioxide. Cobalt was rather less active than Nickel, but much more so than Copper. The products were the same as with Nickel. Iron was similar, being slightly less active than Cobalt. Platinum commenced to react at about 250° C., and split Methyl alcohol almost quantitatively into Carbon monoxide and Hydrogen, without any Methane, and only traces of Formaldehyde. This is the general action of Platinum on alcohols, reaction commencing at about 250° C., at which point the aldehyde formed is almost completely decomposed.

Sabatier's results proved conclusively that the process developed by Trillat and others for the manufacture of Formaldehyde by partial combustion of Methyl alcohol depended upon dehydrogenation; the addition of Oxygen facilitating the reaction by maintaining the Copper in an active state, preventing the reverse reaction by combination with the Hydrogen formed, and reversing the thermal value of the reaction from negative to positive,



Orlov then commenced a series of researches in which Sabatier's results were confirmed and extended. A number of papers in the *Journal of the Russian Physical and Chemical Society* for 1907 and 1908 record the results of Orlov's work, and these have since been collated into two books (see especially "Formaldehyde"). The following catalysts were recommended: Copper, mounted on asbestos or coke, Cerium sulphate, Thoria, Platinum-black, metallic Platinum, and Vanadium pentoxide on asbestos. Iron was unsatisfactory, giving much decomposition to oxides of Carbon and lamp-black. Later Orlov recommended addition of air to the Methyl alcohol vapour, and as catalyst, a short layer of platinised asbestos or pumice, followed by Copper gauze. Under these conditions, the catalyst starts, and continues to work without application of external heat, the "ignition pellets" containing Platinum inducing reaction at the ordinary temperature when the heat generated by the reaction quickly raises the temperature of the whole catalytic mass to working temperature (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 796). The best conversions and autothermic working were obtained observing the following ratios of reactants and space velocity:

Methyl alcohol : Oxygen = 1 : 0.4 or,

Methyl alcohol : Total volume of gaseous mixture = 1 : 3.

$$\frac{[\text{O}_2][\text{CH}_3\text{OH}]}{(\text{Velocity of gas flow})^2} = 0.00103.$$

The investigations were continued by Le Blanc and Plaschke, who showed that metallic Copper and Silver were the most efficient catalysts hitherto used. Spirals of Copper and Silver wire gauze and electrolytically silver covered Copper of various lengths were inserted in a heated tube, and experiments carried out to determine the effect of varying (1) the temperature of the gauze, (2) the air-alcohol ratio, and (3) the length of the gauze spiral (*Z. Elektrochem.*, 1911, 17, 45). When the air-alcohol ratio and the length of the gauze spiral (or space velocity of the reactants) were kept constant, the formation of Formaldehyde was shown to increase as the temperature rose, but secondary destructive actions, such as decomposition to Hydrogen and Carbon monoxide and oxidation beyond the Formaldehyde stage, also increased at the same time. The temperature at which the greatest proportion of the Methyl alcohol reacted in the desired manner was about 450° C., below and beyond which point poorer yields of Formaldehyde were obtained owing to the relatively greater importance of the secondary actions.

For a given temperature and space velocity, the percentage yield of Formaldehyde was a maximum when the air-alcohol ratio was in the following proportions by weight:—

| | | | |
|----------|------------------|----------|--------------------|
| Oxygen : | Methyl alcohol = | 0.46 : 1 | or |
| Air : | Methyl alcohol = | 2.3 : 1 | (Silver catalyst) |
| Oxygen : | Methyl alcohol = | 0.39 : 1 | or |
| Air : | Methyl alcohol = | 2.00 : 1 | (Copper catalyst). |

The loss by secondary actions was least when the proportion of Oxygen was lowest.

In the apparatus used, the maximum yield of Formaldehyde was obtained using a Silver gauze catalyst 7 cm. in length (corresponding apparently with a space velocity of about 3900 litres of air per litre of catalyst space per hour), and amounted to 58.5 per cent. of the Methyl alcohol, 26 per cent. of the Methyl alcohol being recovered unchanged, the loss by decomposition in the experiment amounting to 15.5 per cent. Copper gave slightly less favourable results—the most satisfactory catalyst consisting of a gauze spiral 8–9 cm. long, when the yield of Formaldehyde rose to 55.4 per cent. of the Methyl alcohol, while the Methyl alcohol recovery and the amount decomposed were about the same as before. The minimum loss obtained by decomposition in the whole series of experiments corresponded with 11.76 per cent. of the Methyl alcohol used, the yield of Formaldehyde in the same experiment being 51.4 per cent. The decomposition products always consisted of Carbon monoxide, Carbon dioxide, and Hydrogen, and were obtained in the experiment with a Silver catalyst, referred to above, in the proportions 4.16, 4.46,

and 11.49 per cent., respectively. The process was regarded as consisting essentially in a dehydrogenation of the Methyl alcohol, the Oxygen serving simply to maintain the activity of the catalyst, possibly by alternate oxidation and reduction. When no air was used, or when Nitrogen was used instead, the efficiency of the catalyst continually decreased, becoming rapidly inert.

Fokin passed mixtures of Methyl alcohol vapour and air over metal catalysts heated to various temperatures, and compared the maximum yields obtainable. In general, the yields were highest when the air used contained about the theoretically requisite quantity of Oxygen. The yields obtained were as follows, expressed as percentages of the Methyl alcohol consumed :

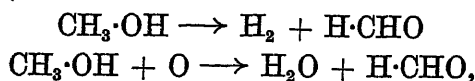
| | | | |
|----------|-----|------------------|-------|
| Ni . . . | 1.1 | Cu . . . | 43.5 |
| Al . . . | 1.5 | Ag . . . | 64.6 |
| Mn . . . | 2.0 | Au . . . | 71.0 |
| Co . . . | 2.8 | CuAg alloy . . . | 84.0. |
| Pt . . . | 5.2 | | |

The action was considered to consist in a direct removal of Hydrogen (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 286).

The efficiency of Silver as a catalyst was also noted by Bouliard (F.P. 412501 of 1910) and Blank (D.R.-P. 228697; F.P. 418349), who recommended mounting it on asbestos fibre.

The Société L'Air Liquide have patented the use of pure Oxygen instead of Air (F.P. 426873 of 1910). A mixture of Methyl alcohol vapour and Oxygen containing considerable excess of the former is led over Copper, deposited upon pumice or other suitable catalyst, heated to start the reaction, which is then regulated by varying the relative proportions of Methyl alcohol and Oxygen, or their rate of passage, in such a way that no appreciable amount of Carbon dioxide is formed. The products are condensed in the usual way, the liquid obtained consisting of Formaldehyde, unchanged Methyl alcohol, and water. More water is added, so that on distilling off the Methyl alcohol a commercial formaline is obtained.

Hochstetter's attempts to obtain a mixed catalyst that would accelerate simultaneously the dehydrogenation and partial combustion processes,



led him to investigate the action of metallic couples, from which he claimed the following percentage yields (E.P. 464 of 1914) :

| | |
|--|----|
| Pure Copper | 70 |
| Copper, alloyed with 1/10,000 Platinum | 72 |
| Copper coated with 1/10,000 Platinum | 77 |
| Silver | 75 |
| Silver, with a Copper tube | 84 |
| Silver, coated with 1/10,000 Rhodium | 96 |
| Silver, coated with 1/10,000 Platinum | 96 |

When metal catalysts are employed, the use of moderately pure rectified Methyl alcohol, containing only water as a considerable impurity, is desirable. The present author has found, however, that if certain mixed oxide catalysts are used, the presence of the usual impurities found in crude wood spirit is of no consequence, and that yields of Formaldehyde can be obtained even greater than can be produced by use of metal catalysts and pure Methyl alcohol. Moreover, in presence of these oxide catalysts, Acetone in the crude wood spirit is destroyed, so that the Methyl alcohol recovered from the product is almost pure. The most satisfactory oxide catalysts consist of combinations of an oxide of Iron, or of a related metal (Cobalt, Nickel, Chromium, or especially Manganese) with a weakly acidic oxide, such as Tungstic, Molybdic, Vanadic, Boric, Phosphoric, Silicic, etc. In such a combination, the highly destructive action of the metallic oxides is much moderated, and Formaldehyde in high yield is obtainable. Such mixed oxide catalysts are made by precipitation between a salt of the metal and a soluble alkali salt of the acid. Thus, Ferric chloride and Sodium tungstate give a yellow precipitate which, when deposited upon a support and washed free from soluble salts, is particularly effective, inducing at a suitable temperature very rapid reaction between pure Methyl alcohol and air almost without simultaneous formation of Carbon dioxide. Using wood spirit, up to 60 per cent. of the Methyl alcohol contained in it is converted into Formaldehyde, while 30 per cent. can be recovered, almost free from Acetone.

Large-scale Manufacturing Plant. The oxidation of Ammonia to Nitric acid and of Methyl alcohol to Formaldehyde are processes possessing much in common from the purely practical point of view, and doubtless the form of catalyst found most satisfactory in the newer process (the oxidation of Ammonia) was suggested by experience gained in the older. The oxidation of Ammonia, essentially a war industry, developed rapidly to an enormous scale, and it is probable that the vast amount of research expended could now be considered in connection with the manufacture of Formaldehyde, where the published data are comparatively meagre. It is unlikely that the manufacture of Formaldehyde has yet attained the high state of efficiency which the newer industry reached in a few years.

Formaldehyde plant consists essentially of: (1) Apparatus for compressing a store of air, and mixing with Methyl alcohol vapour, to form a gaseous mixture of any desired uniform composition. (2) Preheating the mixture, and passing at atmospheric pressure over the contact substance, generally Copper, Silver, or an alloy of the two, in the form of gauze or metal mounted on a suitable support. (3) A separator in which the Formaldehyde produced is condensed and obtained as a 40 per cent. aqueous solution ("Formalin") containing only a little Methyl alcohol, the greater part of which is passed on as vapour to (4) a condenser and scrubbing apparatus, in which the last of the unconverted Methyl alcohol is recovered.

It is essential that Methyl alcohol and air should at no point be brought into contact with heated Iron. Copper, or copper alloys, should always be used.

The Formaldehyde plant at the Formol works of the Côte d'Or, in which wood spirit, obtained by destructive distillation of wood in the Burgundy and Champagne districts, is converted into Formaldehyde, is described by Morel (*J. Pharm. Chim.*, 1905, 21, 177). The wood spirit passes from its storage tank to a mixer constructed on the carburettor principle, where it is vaporised by a current of air, with which it mixes in the desired proportion. The mixture is conducted immediately to the converter, a metal cylinder fitted with longitudinal copper tubes, which are heated to a suitable temperature to bring about the reaction. The tubes are observed through sight holes in the converters, and their temperature is estimated by their colour and glow. The products of the reaction are conducted by a pipe to a good water-cooled coil condenser, attached to which is a receiver in which the crude Formaldehyde solution collects. This is brought to the commercial form by addition of water and removal by distillation of the greater part of the unchanged Methyl alcohol, while the gases issuing from the condenser pass to three scrubbers, in which the last traces of Formaldehyde and Methyl alcohol are extracted.

The more modern Formaldehyde plant of F. H. Meyer, Hannover-Hainholz, is based on Orlov's researches, but includes many improvements in matters of detail, as follows: A compressor maintains a store of air at a constant pressure in a capacious air reservoir, fitted with a pressure gauge and a release valve. Methyl alcohol runs from the store tank into a carburation vessel, where apparatus is arranged to heat the incoming air. This current of air meets a thin stream of Methyl alcohol, and a mixture of air and Methyl alcohol vapour of constant composition is formed, which immediately enters the converter. This is made of Copper and contains the catalyst, usually gauze of Copper, Silver, or Silver-coated Copper, which is maintained at a temperature of 450–500° C. by the heat of reaction. After once

starting, the reaction is easily self-sustaining. The products of the reaction, mainly Formaldehyde, Methyl alcohol, and water, in the vapour state, with Nitrogen and Hydrogen, pass to a separator, in which by a washing process the Formaldehyde is absorbed, and collects as the usual commercial form of Formaldehyde ("Formalin"), a 38-39 per cent. aqueous solution containing a small quantity of Methyl alcohol, which at the concentration is necessary to prevent solid Paraformaldehyde separating on standing. The main bulk of the unchanged Methyl alcohol in the reaction product passes on, and is condensed, the last traces being finally removed by thorough water scrubbing. The condensed Methyl alcohol is pumped back to the storage tank, which feeds the carburettor, while the dilute Methyl alcohol obtained from the scrubbers is first concentrated by fractionation.

Preparation of Acetaldehyde

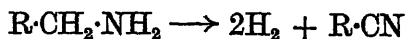
The addition of air to Alcohol vapour is not in this case necessary. A simple laboratory apparatus capable of preparing several kilos. per day of Acetaldehyde is constructed as follows: Methylated spirit, from which the greater part of the water has been removed by fractionation, is vaporised in a Copper boiler, and the vapours are led through a Copper preheater tube to a Copper tube containing the catalyst, both preheater and catalyst being maintained at 280-350° C. The catalyst is conveniently prepared by soaking pumice in a strong solution of Copper formate, drying and inserting in the tube. At a temperature considerably below 280° C., the formate decomposes into a clean and active surface of metallic Copper, and the Alcohol vapour can be immediately introduced. The products of the reaction pass directly to a long ice-cooled coil condenser, where the greater part of the unchanged Alcohol and Aldehyde is condensed, while the remainder is collected by passing the exhaust Hydrogen up towers packed with ice—where the Alcohol and Acetaldehyde dissolve to aqueous solutions on the surface of the ice, and are caught in a receiver below. Almost pure Hydrogen remains. The Aldehyde, Alcohol, and water are separated by fractionation, preferably after "fixing" the Aldehyde, as, for example, Aldehyde-Ammonia, and the Alcohol is again used in the reaction. The Copper catalyst requires periodic activation. This is accomplished by oxidation with air, when all organic impurities are burned away. Alcohol vapour is then introduced to the oxidised surface, some being consumed in reducing the oxide back to the metal before the normal dehydrogenation recommences.

Palmer has shown that, although Alcohol is almost quantitatively dehydrogenated to Aldehyde and Hydrogen by Copper below 300° C., if the products of the reaction, Hydrogen and Acetaldehyde, are

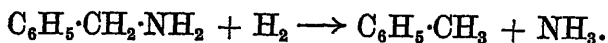
passed over catalytic Copper at 270–290° C., much decomposition and resinification occur. "Protective poisoning" of the Copper by an adsorbed layer of Alcohol was supposed to occur when Alcohol was dehydrogenated in presence of Copper (see page 32) and the reaction was supposed to proceed in three stages: (1) Adsorption of Alcohol by the catalyst. (2) Activation of certain Alcohol molecules by absorption of energy. (3) Evaporation of Aldehyde and Hydrogen from the catalyst in a stream of Alcohol vapour (*Proc. R.S.*, 1920, ✓ 98*A*, 13).

Dehydrogenation of Amines

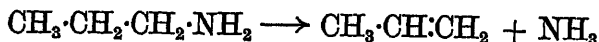
The formation of amines by hydrogenation of nitriles was first described by Sabatier and Senderens in 1905 (*C.R.*, 1905, 140, 482). Sabatier and Gaudion have since shown that when primary amines are passed alone over Nickel at a higher temperature, 300–350° C., the reverse change occurs, and the main products are the corresponding nitriles,



(*C.R.*, 1917, 165, 224). Thus, Benzylamine, $C_6H_5 \cdot CH_2 \cdot NH_2$, gave mainly Benzonitrile, $C_6H_5 \cdot CN$, with smaller quantities of Toluene and Ammonia, and isoAmylamine, $(CH_3)_2CH \cdot CH_2 \cdot CH_2 \cdot NH_2$, gave iso-Valeronitrile, $(CH_3)_2CH \cdot CH_2 \cdot CN$, together with smaller and varying amounts of isoPentane and Ammonia, the former of which further decomposed in contact with the Nickel. The formation of hydrocarbon and Ammonia was due to hydrogenation of amine effected by the Hydrogen split off in the main reaction,



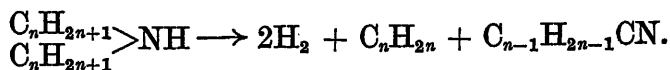
Attempts to obtain Hydrocyanic acid by dehydrogenation of Methylamine were unsuccessful, probably owing to anticatalytic action of Hydrocyanic acid on Nickel. The other lower primary amines, Ethylamine, the Propylamines, and the Butylamines also gave unsatisfactory results in the reaction, owing in their case to the tendency of Nickel to split off Ammonia, with formation of the olefinic hydrocarbons:



(Sabatier and Gaudion, *C.R.*, 1917, 165, 310). Copper was not a satisfactory substitute for Nickel in any of these cases, since the reaction it induced was a much more complex one.

The dehydrogenation of secondary and tertiary amines was carried out independently by Mailhe and de Godon (*C.R.*, 1917, 165, 557) and by Mailhe (*C.R.*, 1918, 166, 996). In the vapour phase,

with Nickel at 350–380° C., dehydrogenation of secondary amines followed a similar course to that of the primary, a nitrile being formed, while the residual hydrocarbon groups were split off as olefinic hydrocarbons, thus :

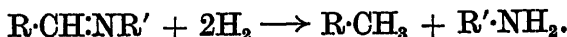


In this way, Di- and Tri-propylamines, $(\text{C}_3\text{H}_7)_2\text{NH}$ and $(\text{C}_3\text{H}_7)_3\text{N}$, both gave Propionitrile and Propylene; Di- and Tri-butylamines, $(\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{NH}$ and $(\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2)_3\text{N}$, gave Butyronitrile, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN}$ and Butylene; Di- and Tri-amylamines, $(\text{CH}_3(\text{CH}_2)_4)_2\text{NH}$ and $(\text{CH}_3(\text{CH}_2)_4)_3\text{N}$, gave Valeronitrile, $\text{CH}_3\cdot(\text{CH}_2)_3\cdot\text{CN}$, and Pentene; Di-isoamylamine,



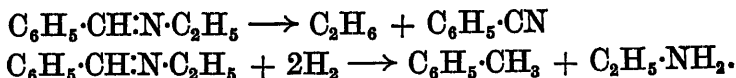
with Nickel at 320–330° C., gave isoValeronitrile, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CN}$, and Amylene, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}\cdot\text{CH}_2$, while the two Hexylamines, $(\text{CH}_3(\text{CH}_2)_4\cdot\text{CH}_2)_2\text{NH}$ and $(\text{CH}_3(\text{CH}_2)_4\cdot\text{CH}_2)_3\text{N}$, gave Hexonitrile, $\text{CH}_3(\text{CH}_2)_4\cdot\text{CN}$, and Hexylene, $\text{CH}_3(\text{CH}_2)_3\cdot\text{CH}\cdot\text{CH}_2$.

Schiff's Bases. The behaviour on dehydrogenation of Schiff's bases, which may be regarded constitutionally as partially dehydrogenated secondary amines, is analogous. Mailhe has shown that in the hydrogenation of Schiff's bases to amines (see page 220), with Nickel at 200–250° C., a secondary reaction always occurs, in which part of the base ruptures at the double bond into two residues, which hydrogenate separately to a hydrocarbon and a primary amine,

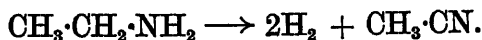


This reaction becomes the predominant one at a higher temperature, even when the base is passed over the catalyst without Hydrogen, the Hydrogen necessary for the reaction being obtained by dehydrogenation to nitrile (*Bull. Soc. chim.*, 1920, IV, 27, 229).

Benzylidene ethylamine, $\text{C}_6\text{H}_5\cdot\text{CH}\text{:N}\cdot\text{C}_2\text{H}_5$, passed over Nickel at 420° C., splits first at the double bond in the two possible ways as follows :—



The products of these primary actions are then partially decomposed, part of the Toluene giving Benzene, Carbon, and Hydrogen, the Ethane "cracking" into Methane, Carbon, and Hydrogen, and the Ethylamine dehydrogenating to Acetonitrile,



These decompositions furnish the Hydrogen necessary for the second of the reactions represented above, which, in practice, is always the predominating one.

The following Schiff's bases were also dehydrogenated by Mailhe. Benzylidene ortho-toluidine, $o\text{-CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_5$, with Nickel at 420–430° C., gave ortho-Toluidine, Toluene, Benzene, a little ortho-Tolunitrile, Carbon, Hydrogen, and possibly some of the secondary amine, $o\text{-CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$, by hydrogenation of the original base. Benzylidene aniline, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_5$, with Nickel at 450° C., gave Toluene, Benzonitrile, Aniline, Benzene, Carbon, and Hydrogen. isoPropylidene aniline, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_5$, gave Benzene, Aniline, isoButyronitrile, Carbon, Hydrogen, and Ammonia. isoButylidene aniline, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_5$, and isoButylidene ortho-toluidine, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$, with Nickel at 430° C., gave analogous products.

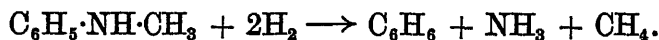
Finely-divided Copper was much less effective, and the activity of the Nickel was short-lived on account of the deposition of Carbon.

Aromatic Amines and Alkyl Anilines. Aromatic amines such as Aniline are unable to undergo dehydrogenation to nitriles, and are remarkably stable in presence of hot catalytic metals. Thus, Sabatier and Gaudion have shown that Aniline, the Toluidines, and Xylidines, when passed alone over heated Nickel, are almost unattacked at 350° C., and that a temperature of 500° C. is required to decompose them completely into Ammonia, Carbon, and the aromatic hydrocarbon.

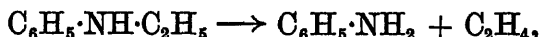
Amines substituted in the amido-group, however, are not so stable, the substituent being easily eliminated by contact with Nickel at 350° C., and the stable parent amine produced in good yield. Thus, Methyl aniline and Dimethyl aniline give chiefly Aniline, together with Carbon, Methane, Benzene, and Ammonia, and the Ethyl anilines behave similarly, Aniline again being the chief product (*C.R.*, 1917, 165, 309). The mechanism is as follows: The principal action is



the Hydrogen then in part effecting the well-known hydrogenation,

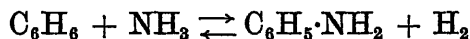


Ethyl aniline similarly gives



whereupon the Ethylene decomposes in the usual way to Carbon, Methane, Ethane, and Hydrogen, the last-named then hydrogenating the amine as before.

Dehydrogenation between Benzene and Ammonia. A small yield of Aniline has been claimed by Meyer and Tauzen by passing a mixture of Benzene vapour and Ammonia through a tube heated to 550° C., the action being reversible,

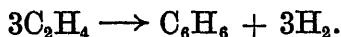


(*Ber.*, 1913, 46, 3183).

Wibaut was led to reinvestigate this reaction by the consideration that Sabatier and Senderens had shown that, in contact with Nickel, Cobalt, or Iron, the reverse action easily occurred at temperatures above 250° C. Accordingly, Benzene vapour and Ammonia were passed through a porcelain tube at temperatures up to 700° C. No appreciable quantity of Aniline was produced. When, however, finely-divided Iron or Nickel, mounted on asbestos and heated to 550° C., was employed as catalyst then traces of Aniline were obtained. Thus, Ammonia gas, saturated with Benzene vapour, was passed through an iron tube packed for 60 cm. of its length with the above catalyst, when, after 200 c.c. of liquid reaction products had been condensed, it was found that 0.11 gram of Aniline (identified as Acetanilide) had been formed (*Ber.*, 1917, 50, 541).

These experiments were again repeated by Briner, Ferrero, and Luserna, who pointed out that dehydrogenation between Benzene and Ammonia would be an endothermic reaction. Traces only of Aniline were obtained (*Helv. Chim. Acta*, 1924, 7, 282).

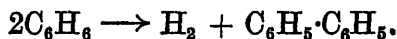
Fusion of Aromatic Nuclei by Dehydrogenation. It has already been shown that aromatic bodies are among the products obtained when complex open-chain compounds are subjected to pyrogenous decomposition. Owing to the remarkable stability of the aromatic ring, benzene derivatives may even be formed by heat treatment of simpler compounds, such as Acetylene and Acetone, which polymerise or otherwise react, giving respectively Benzene and Mesitylene. Ipatiev showed that Ethylene and Propylene under high pressure similarly underwent condensation, one of the main reactions being



This reaction was shown to be powerfully catalysed by anhydrous inorganic chlorides, especially Aluminium chloride and Zinc chloride, when action became rapid at 200–300° C.

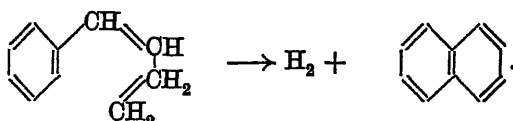
On account of this extreme stability of aromatic compounds, exposure to a high temperature effects very different results from those obtained with open-chain compounds, though the primary action may be one of dehydrogenation in both cases. Benzene vapour when passed through a red-hot tube combines to Diphenyl,

parting with one atom of Hydrogen from each of the uniting nuclei,

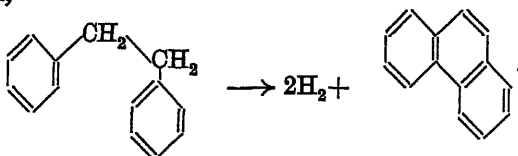


Toluene similarly gives a complex mixture of isomeric Ditolyls, and other Benzene and Naphthalene hydrocarbons behave in the same way.

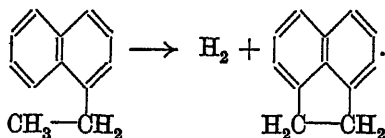
Compounds constituted by a fusion of aromatic nuclei are even stabler than monocyclic aromatic compounds, and therefore tend to be formed with increasing ease, though not, except in occasional instances, in high yields. Thus, many substances and mixtures of substances, simple or complex, when passed through a red-hot tube, yield Naphthalene, Phenanthrene, Anthracene, Acenaphthene, and similar condensed hydrocarbons—this fact accounting for their presence in tar formed by high temperature carbonisation of coal. Very many mixtures (*e.g.*, Toluene vapour and Ethylene) on pyrogenous treatment yield small quantities of Naphthalene. Liebermann and Riiber obtained Naphthalene easily by simple dehydrogenation in a hot tube of α -Phenyl $\alpha\gamma$ -butadiene (*Ber.*, 1902, 35, 2697),



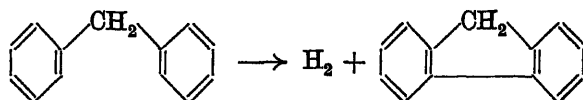
Condensation to Anthracene has been shown to occur in some measure when Toluene vapour (Berthelot, *Bull. Soc. chim.*, 1867, (2), 7, 218), or a mixture of Benzene vapour and Ethylene (Berthelot, *ibid.*, 276; *Ann.*, 1867, 142, 257) are passed through a red-hot porcelain tube. Phenanthrene has been obtained similarly from Toluene (Graebe, *Ber.*, 1874, 7, 48), from a mixture of Diphenyl vapour and Ethylene (Barbier, *Ann. Chim. Phys.*, 1876, (5), 7, 532), and easily from Dibenzyl,



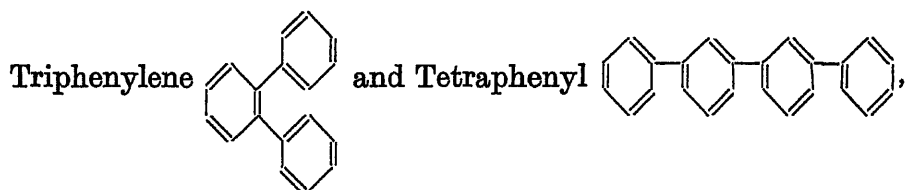
Acenaphthene is easily formed in the same way from α -Ethyl naphthalene,



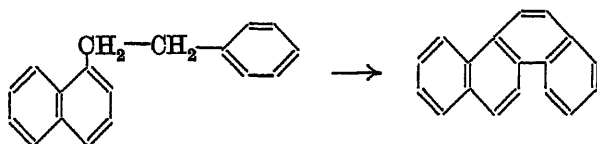
Fluorene from Diphenyl methane,



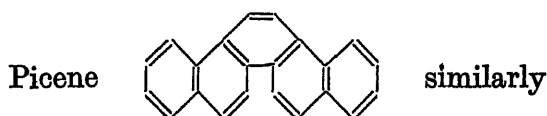
(Graebe, *Ber.*, 1874, 7, 1624; *Ann.*, 1874, 174, 194),



from Diphenyl and other substances (Schmidt and Schultz, *Ann.*, 1880, 203, 134), Chrysene from Indene (Spilker, *Ber.*, 1893, 26, 1544) and from Benzyl α -naphthyl methane,



(Bungener and Graebe, *Ber.*, 1879, 12, 1079), and

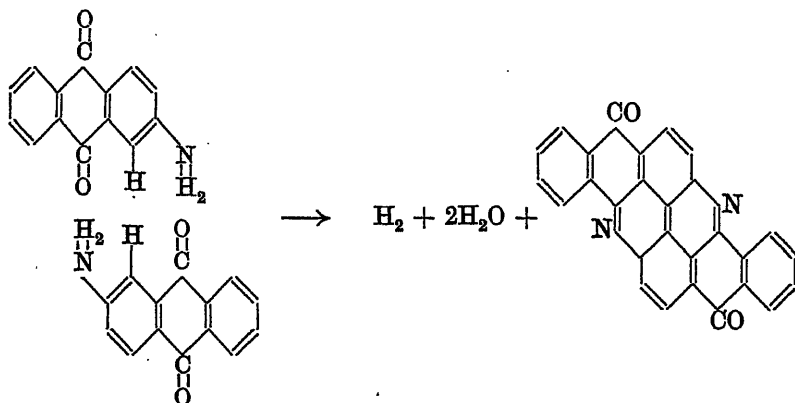


(Hirn, *Ber.*, 1899, 32, 3341).

This type of dehydrogenation is much facilitated by Aluminium chloride and other anhydrous inorganic halides (Aluminium bromide, Ferric chloride or bromide, Zinc chloride, etc.), which function as true catalysts, just as in the McAfee process for degradation of hydrocarbons. Scholl and his co-workers, by the use of Aluminium chloride, have prepared many new, highly-condensed polynuclear compounds, in some cases in high yields.

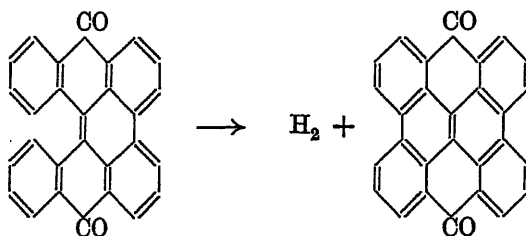
The first reaction of this type was observed by Scholl, who found that anhydrous Aluminium chloride was among those reagents that by simultaneous dehydration and dehydrogenation effected the

condensation of two molecules of β -Amino anthraquinone to Flavanthrene (*Ber.*, 1907, 40, 1691; D.R.-P. 138119):—



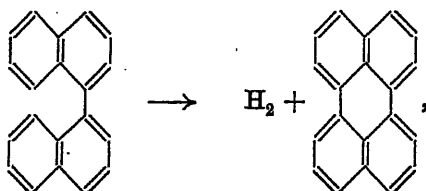
The same reaction was induced, but was assisted by oxidation, when the β -Amino anthraquinone was fused with caustic Potash (D.R.-P. 136015), heated with Antimony pentachloride in Nitrobenzene solution (D.R.-P. 139633), or heated with an acid oxidiser such as Chromic acid (D.R.-P. 141355). The constitution of Flavanthrene was established by synthesis.

Scholl and Mansfield then condensed mesoBenzodanthrone almost quantitatively to mesoNaphthodanthrone, under the influence of anhydrous Aluminium chloride at 140°C .



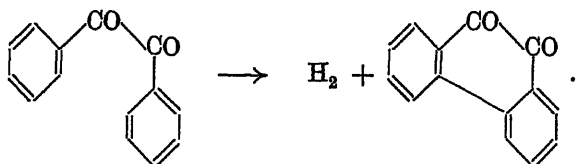
(*Ber.*, 1910, 43, 1734).

Scholl, Seer, and Weitzenbock effected the condensation of $\alpha\alpha'$ -Dinaphthyl to Perylene,

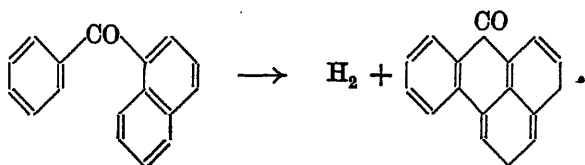


the constitution of which was established by synthesis from Naphthalene 1 : 8-diamine (*Ber.*, 1910, 43, 2203). This reaction was shown to occur with much decomposition when the Dinaphthyl vapour was simply passed through a red-hot tube. In presence of anhydrous Aluminium chloride, however, the reaction commenced at 80° C., proceeded with formation of a high yield at 140–145° C., and extremely rapidly at 180° C.

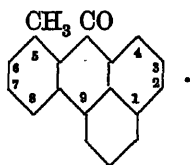
Aromatic ketones especially were shown by Scholl and Seer to dehydrogenate to condensed ring systems when heated alone with anhydrous Aluminium chloride (*Sitz. Akad. Wien*, 1911, 120, 11 B, 925; E.P. 16271 of 1911; D.R.-P. 239761; *Monats.*, 1912, 33, 1; *Ann.*, 1912, 394, 111). Thus, Benzil, $C_6H_5 \cdot CO \cdot CO \cdot C_6H_5$, below 100° C. gave an almost quantitative yield of Phenanthraquinone,



Aromatic mono- or di-ketones, possessing a free peri-position with respect to a carbonyl group, at about 140–150° C. under the influence of the anhydrous chlorides or bromides of Aluminium or Iron often condensed to Benzanthrone or Pyranthrone derivatives. Thus when 1 part of Phenyl α -naphthyl ketone was heated with 5 parts of Aluminium chloride to 150° C. for 2½ hours, a 76 per cent. yield of Benzanthrone was produced,

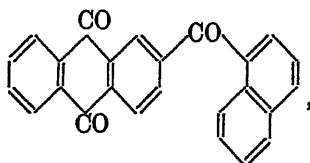


Substituted Phenyl α -naphthyl ketones gave derivatives of Benzanthrone, thus α -Naphthyl ortho-tolyl ketone, heated to 120–130° C. for 1½ hours with 5 parts of Aluminium chloride, gave 5-Methyl benzanthrone,

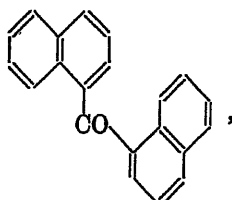


Naphthyl meta-tolyl ketone, after 5 hours' heating at 140°C ., gave 6-Methyl benzanthrone, and similarly

α -Naphthyl para-tolyl ketone,
 α -Naphthyl para-diphenyl ketone, $\text{C}_{10}\text{H}_7\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_5$,
 4-Hydroxy α -naphthyl phenyl ketone,
 2-Anthraquinolyl α -naphthyl ketone,

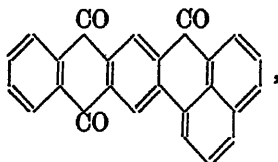


and $\alpha\alpha'$ -Dinaphthyl ketone,

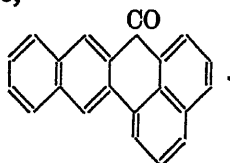


gave, respectively,

7-Methyl benzanthrone,
 7-Phenyl benzanthrone,
 2-Hydroxy benzanthrone,
 6 : 7-Phthaloyl benzanthrone,

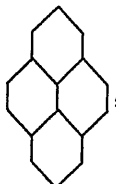


and Naphthabenzanthrone,



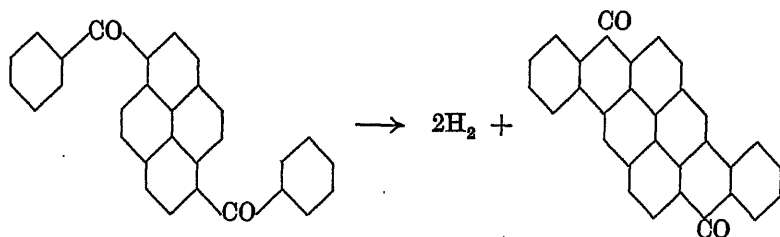
The Benzoyl pyrenes, and homologous bodies similarly condensed

gave Pyranthrones. When Pyrene,



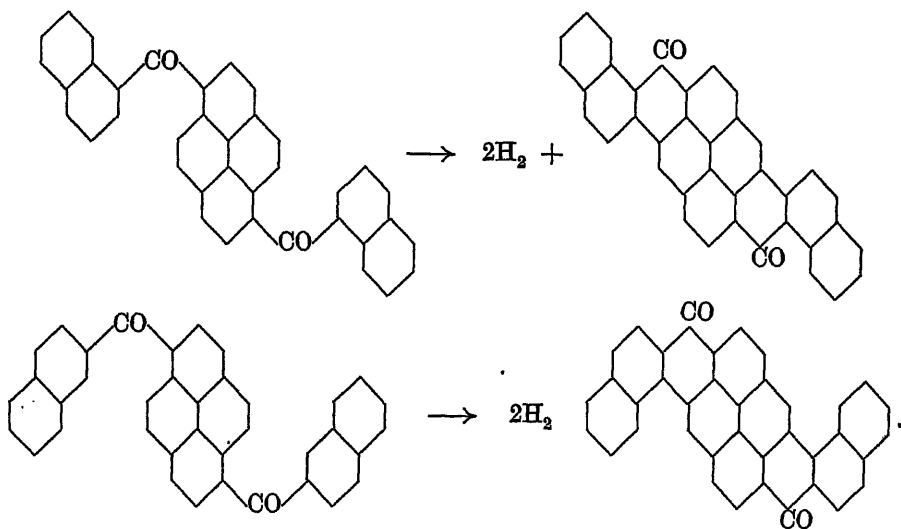
Benzoyl chloride in presence of anhydrous Aluminium chloride

(Friedel-Crafts' reaction), a mixture of the 3:8-Dibenzoyl and 3:5:8-Tribenzoyl pyrenes was formed, which could be resolved into its constituents by fractional crystallisation from Acetic acid. The former, Dibenzoyl pyrene, when heated rapidly to 155–160° C. with anhydrous Aluminium chloride and maintained for 1 hour, gave a good yield of Pyranthrene,



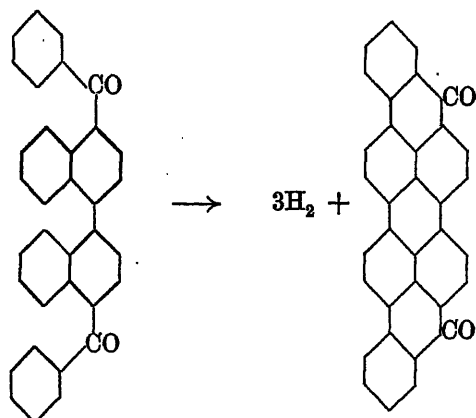
When the Dibenzoyl pyrene was heated slowly to the reaction temperature, benzoyl groups tended to be eliminated at a relatively greater rate than ring closure occurred, and the yields of Pyranthrene were reduced. 3:5:8-Tribenzoyl pyrene in the same way first condensed to 3-Benzoyl pyranthrene, which at a slightly higher temperature (165–170° C.) rapidly lost its benzoyl group, yielding Pyranthrene.

The di- α - and di- β -Naphthoyl pyrenes similarly condense to the corresponding Naphthapyranthrones (Dibenz-pyranthrones), thus

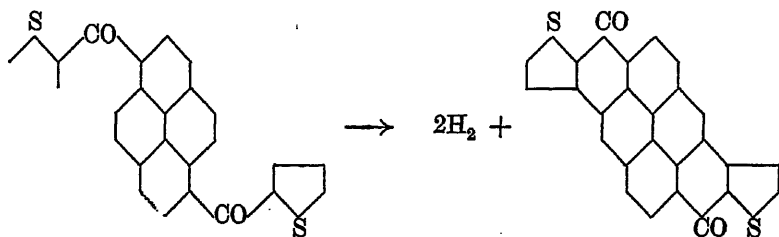


In the same way, 4:4'-Dibenzoyl $\alpha\alpha'$ -dinaphthyl (made by the Friedel-Crafts reaction from α -Dinaphthyl and Benzoyl chloride, by

heating in presence of anhydrous Aluminium chloride) when heated with anhydrous Aluminium chloride gave Violanthrene,



Heterocyclic nuclei were found similarly to condense. Furane derivatives gave indefinite, tarry products, but from Thiophene was obtained 3 : 8-Di-thiophenoyl pyrene (analogous with 3 : 8-Dibenzoyl pyrene), which on heating alone with anhydrous Aluminium chloride parted with Hydrogen in the same way as Dibenzoyl pyrene, forming the Thiophene analogue of Pyranthrone, Benzthiophanthrone,

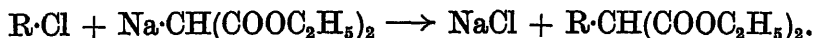


CHAPTER XI

DEHYDRATION

Introduction. Classification of Dehydrating Catalysts and Dehydration Reactions. Sabatier's Theory of Catalytic Dehydration. Dehydration of Alcohols: (a) Formation of Ethers; Dimethyl Ether, Ether, β -Naphthol Ethyl Ether; (b) Formation of Unsaturated Hydrocarbons, and Manufacture of Ethylene; (c) Dehydration of Polyhydric Alcohols. Formation of Amines by Dehydration. Formation of Alkylanilines. Dehydration between Alcohols and Acids: (a) Sulphuretted Hydrogen; (b) Halogen Acids; (c) Organic Acids. Action of Dehydrating Catalysts on Esters. Action between Esters and Amines (including Ammonia) in Contact with Dehydrators. Action between Carbon Monoxide and Ammonia, and Formation of Cyanides. Action between Carbonyl Compounds and Ammonia. Dehydration of Oximes. Hydrolysis of Amides and Nitriles. Crotonisation. Ring Formation by Dehydration.

THE vast majority of simple organic reactions can be classed roughly as "Oxidations," "Reductions," "Additions," "Substitutions," or "Condensations." The last term implies a reaction between two compounds accompanied by elimination of a simple inorganic molecule, such as water, Hydrochloric acid, etc., for example:—



The tendency for such condensations to occur is greater the higher the heat of formation of the molecules formed by the exchange, since the thermal value of the reaction is thereby enhanced. Reactions involving the splitting off of water should therefore be common, on account of the high heat of formation of water, an expectation amply realised in organic chemistry. Such reactions are termed "Dehydrations," and are very susceptible to the action of catalysts. Dehydrating catalysts comprise a wide variety of different substances classified by Sabatier as follows:—

1. Elementary, or simple bodies, such as Phosphorus, Carbon, or finely-divided metals.
2. Mineral acids, especially Phosphoric, Sulphuric, and the halogen acids, either concentrated or dilute.
3. Acid anhydrides, such as Phosphoric, P_2O_5 , or Boric, B_2O_3 .

4. Anhydrous chlorides, such as those of Aluminium, Iron, and Zinc.

5. Inorganic salts possessing an affinity for water, such as some Ammonium salts, Potassium hydrogen sulphate, Calcium sulphate, Aluminium sulphate, phosphates, etc.

6. Organic acids, such as acetic, and their salts, such as Sodium or Potassium acetates.

7. Dehydrating oxides.

Dehydration reactions may be classified as follows:—

1. Dehydration of alcohols to ethers or olefines.

2. Dehydration of phenols to phenolic ethers and phenylene oxides.

3. Dehydration between an alcohol or a phenol, and a second substance:—

(a) A second alcohol, to give a mixed ether.

(b) Ammonia, or primary or secondary amines, to give primary, secondary, or tertiary amines, respectively.

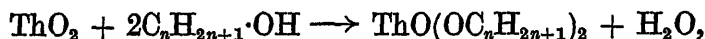
(c) Sulphuretted hydrogen to give mercaptans and sulphides.

(d) Acids, organic or inorganic, to form esters.

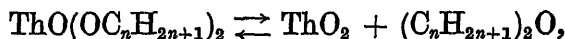
4. "Condensation" reactions, such as the Aldol condensation, and the Claisen reaction.

These general types include by far the greater number of dehydrating reactions, but not all. These will be considered separately.

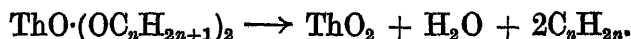
Sabatier and Mailhe advocated the chemical theory of catalysis to explain all these types of reactions, even in those cases where an oxide at a high temperature was used as a contact agent (*C.R.*, 1910, 150, 823). The formation of intermediate compounds when mineral acids, or anhydrous chlorides, were used as dehydrating agents has been established by researches dating from the time of Williamson. When Thoria or Alumina is used, Sabatier and Mailhe considered that the alcohol first reacted with the oxide as follows:—



and that the metallic complex could then decompose in two ways : at low temperatures giving an ether,

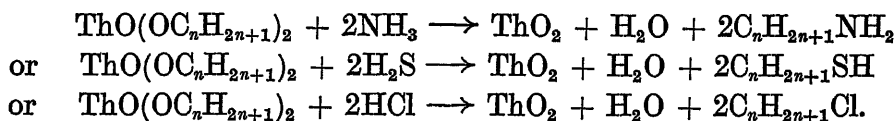


or at a high temperature giving an olefine,



Since ethers can be dehydrated to olefines, the first of the above reactions must be considered to be reversible.

The same mechanism was regarded as explaining the dehydration that occurs when an alcohol vapour is led with Ammonia, Sulphuretted hydrogen, Hydrochloric acid, or other substance over a suitable catalyst. Thus, in presence of these bodies, the above decompositions of the metallic complex are more or less completely suppressed, which reacts instead as follows :—

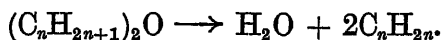


Dehydration of Alcohols

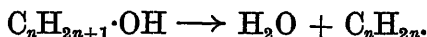
Alcohols can be dehydrated in two stages. In the first stage an ether is formed :—



This, by further dehydration, yields an olefinic hydrocarbon :—



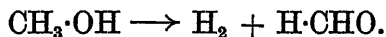
Very commonly, the two stages of the reaction cannot be separated, and dehydration proceeds directly to the formation of the olefine,



Methyl alcohol, on the other hand, which cannot give an olefine, undergoes dehydration only to Dimethyl ether,



a reaction that can be effected by use of a large choice of catalysts. At the same time, dehydrogenation with formation of Formaldehyde is more prone to occur than with other alcohols,

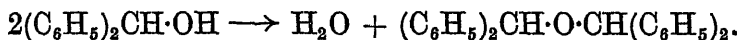


Thus, in contact with oxides of Glucinum, Zirconium, Zinc, Uranium, Molybdenum, Vanadium, Lead, Tin, Cadmium, or Iron, the predominating reaction with Methyl alcohol is dehydrogenation, with greater or less decomposition of the Formaldehyde formed into Carbon monoxide and Hydrogen (Sabatier and Mailhe, *C.R.*, 1919, 148, 1734).

The two stages of dehydration are most easily isolated in the case of the primary alcohols, but the two stages become less easy to separate as the complexity of the alcohol increases. For example, Methyl alcohol dehydrates exclusively to the ether. Ethyl alcohol gives nearly pure ether or nearly pure olefine, according to the

catalyst and conditions employed. Propyl alcohol always gives much Propylene, and as the series is further ascended, the formation of ether occurs in progressively diminishing yields.

Secondary alcohols dehydrate more easily than the primary, but as a rule give only the olefine. Benzhydrol is a noteworthy exception, very easily giving the corresponding ether in high yield, even in contact with catalysts which are usually regarded as dehydrogenating (*e.g.*, Copper),

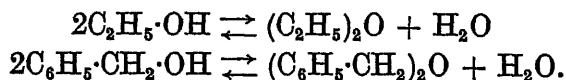


Tertiary alcohols never yield an ether by dehydration, but very easily give the corresponding unsaturated hydrocarbon.

Dehydrations can frequently be reversed. For example, in presence of Thoria, Phenol and Ethyl alcohol vapours give Phenyl ethyl ether, $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{C}_2\text{H}_5$. Mailhe has shown that when Phenyl ethyl ether and steam are vaporised over Thoria at 460°C ., the product condenses to two liquid layers, one containing water, giving a strong aldehyde reaction, the other an oily layer, containing unchanged ether and Phenol. In the same way, Dimethyl aniline, $\text{C}_6\text{H}_5\cdot\text{N}(\text{CH}_3)_2$, which is formed by dehydration between Aniline and Methyl alcohol, when passed with excess of steam over a dehydrating catalyst, hydrates back to Aniline and Methyl alcohol, with simultaneous formation of Formaldehyde from the latter (*Caoutchouc et Guttapercha*, 1920, 17, 10584; *Chem. Abs.*, 1921, 15, 524). The reversibility of dehydrating reaction was also proved by Ipatiev, who showed that the decomposition of alcohols in presence of dehydrating oxide catalysts, *e.g.*, Alumina, was diminished by application of pressure. He noted, in consequence, that under pressure it was necessary to employ a higher temperature to effect dehydration. In all such cases, when Alumina was used as the catalyst, at temperatures rather below the point necessary to effect decomposition to olefine, the formation of ether was observed. The direct recombination of ether and water to alcohol, under the action of Alumina, also was established (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 813; 1906, 38, i, 63, 75, 92; *Ber.*, 1904, 37, 2986).

The Formation of Ethers

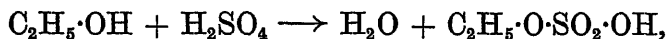
The production of ethers by dehydration of alcohols is practically restricted to the simpler primary alcohols (including aromatic alcohols, like Benzyl alcohol), and the choice of catalysts that effect this partial dehydration is more limited than when the complete dehydration to olefine is sought:



Higher primary alcohols and secondary alcohols (except in the unique instance of Benzhydrol) give inferior yields of ether, or none at all, while from tertiary alcohols the ethers are never obtainable.

Elementary Substances as Catalysts. Simple substances, such as charcoal, red Phosphorus, or finely-divided metals, do not dehydrate alcohols to ethers except in the single instance of Benzhydrol, which in contact with Copper gives the ether, $(C_6H_5)_2CH \cdot O \cdot CH(C_6H_5)$ (Knoevenagel and Heckel, *Ber.*, 1903, 36, 2823). Only the olefines, or the dehydrogenation reaction, can be obtained using these catalysts.

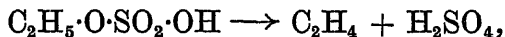
Mineral Acids as Catalysts. For the production of ethers, mineral acids, especially Sulphuric and Phosphoric, are the most useful catalysts (Dumas and Peligot, *Ann. Chem. Phys.*, 1835, (2), 58, 19; Williamson, *ibid.*, 1854, (3), 40, 98). The mechanism of this reaction was elucidated in Williamson's classical research. Ethyl sulphuric acid was isolated as an intermediate product at low temperatures,



and shown to decompose at higher; at $140^\circ C.$, in presence of excess of Alcohol, almost exclusively into Ether,



and at still higher temperatures into Ethylene,



regenerating the Sulphuric acid in each case. This explanation has been confirmed by preparing Amyl sulphuric acid, and reacting upon this substance with Ethyl alcohol, when Amyl ethyl ether, $C_5H_{11} \cdot O \cdot C_2H_5$, was obtained (see also Prunier, *J. Pharm. Chim.*, 1897, 5, 513).

Theoretically, therefore, a small amount of Sulphuric acid should effect the transformation of indefinite quantities of Alcohol. In practice, however, a small proportion of the acid is continuously reduced to Sulphur dioxide by the action of the Alcohol, which itself is converted into tarry products and Carbon. The acid must therefore be replenished at intervals, and the action periodically stopped for cleaning. Syrupy Phosphoric acid, which is quite as powerful a dehydrant, does not undergo reduction or cause charring, and can be used for a very long time without renewal (Sabatier and Mailhe, *Bull. Soc. chim.*, 1907, (4), 1, 524).

Senderens has shown that the mineral acid in these dehydrations functions as a true catalyst, and that the large quantity often required is necessary merely to raise the boiling point of the mixture to the temperature of reaction. This being so, the reaction is independent of the quantity or concentration of acid (these factors merely affecting

the speed with which it takes place), except in so far that a large quantity, or a high concentration, is the most convenient method of rendering possible the attainment of the necessary temperature, without application of pressure (*C.R.*, 1923, 176, 813). For example, a mixture of 100 c.c. of Propyl alcohol with 75 c.c. of strong Sulphuric acid boils at 140° C., and gives Propylene almost exclusively. If the quantity of acid is reduced to 40 c.c., the boiling point is about 125° C., and 30 per cent. of the Propyl alcohol can be converted into Propyl ether. Other mixtures of alcohol and acid boiling about the same temperature give almost identical products; thus, a mixture of 100 c.c. of Propyl alcohol with 200 c.c. of $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ boils at about 135° C., and gives Propylene. When the amount of $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ is reduced to 60 c.c., the mixture boils at 125° C., and a 38 per cent. yield of Propyl ether is obtainable. Similarly Propyl alcohol mixed with one-third of its volume of $\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$ boils at 125° C., and gives a 40 per cent. yield of Propyl ether.

Methyl alcohol is by far the easiest of the alcohols to dehydrate, on account of the absence of the usual complication, viz., dehydration to olefine. In presence of Sulphuric or Phosphoric acid, over a wide range of temperature, it is dehydrated quantitatively to Dimethyl ether.

Ethyl alcohol can similarly be dehydrated almost quantitatively to ordinary Ether, but the range of temperature over which this is the exclusive reaction is a rather narrow one, since below 130° C. reaction is slow, and above 150° C. dehydration to Ethylene becomes very pronounced. Any non-volatile acid, *e.g.*, Sulphuric, Phosphoric, or Arsenic (Boullay, *Gilbert's Ann.*, 1913, 44, 270), can be used.

Propyl alcohol can similarly be dehydrated to Dipropyl ether with strong Sulphuric acid, but even at the lowest working temperature more than half the Propyl alcohol undergoing change yields Propylene.

Higher alcohols than Propyl alcohol, *e.g.*, isoButyl alcohol, are stated not to give ethers under the action of strong mineral acids as catalysing agents, only the olefine being formed (Norton and Prescott, *Amer. Chem. J.*, 1884, 6, 243). Adams, Kamm, and Marvel, however, during the preparation of Amylene from isoAmyl alcohol, by the action of hot strong Sulphuric acid, obtained large quantities of isoAmyl ether (*J. Am. C.S.*, 1918, 40, 1950).

Alcohols which yield ethers by this reaction can, when used together, be made to yield a certain proportion of the mixed ether; for example, a mixture of Methyl and Ethyl alcohols with strong Sulphuric acid at 140° C. gives in addition to Dimethyl and Diethyl ethers (chiefly) a certain amount of Methyl ethyl ether. Ethyl propyl ether can be similarly formed, and also Ethyl isoamyl ether (Peter, *Ber.*, 1899, 32, 1419), but Ethyl isobutyl ether, it is

said, cannot. Tertiary Butyl-ethyl ether, $(\text{CH}_3)_3\text{C}\cdot\text{O}\cdot\text{C}_2\text{H}_5$, was made by Mamontov by heating a mixture of tertiary Butyl and Ethyl alcohols with 2 per cent. of their volume of strong Sulphuric acid in a sealed tube at 100°C . for 5 hours (*J. Russ. Phys. Chem. Soc.*, 1897, 29, 234). It would therefore appear that the Sulphuric acid method of etherification is more general for preparation of aliphatic ethers than is generally recognised, the formation of the ether being largely a question of temperature, and the method of isolation by distillation depending upon a temperature of reaction at which the ether is volatile.

Phenols when heated with a mineral acid and alcohol do not give the phenolic alkyl ether, since a higher temperature is necessary for the formation of these compounds than is the case with the aliphatic ethers. A temperature of at least 150°C . in an autoclave is necessary to prepare Anisole, $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{CH}_3$, from Phenol and Methyl alcohol, in which case Potassium bisulphate is a more satisfactory dehydrant. Naphthols, on the other hand, yield alkyl ethers with relative ease when heated with a mineral acid and an alcohol. The only product is the mixed Naphthyl-alkyl ether, none of the simple dialkyl or dinaphthyl ethers being formed. The naphthol is added to excess of the alcohol, and heated to $125\text{--}140^\circ\text{C}$. for some hours with 15 to 25 per cent. of the weight of the mixture of strong Sulphuric acid. The product is isolated by pouring into excess of water, and purified by extracting unchanged Naphthol with hot dilute caustic Soda, and distilling (Gattermann, *Ann.*, 1888, 244, 72; Davis, *J.C.S.*, 1900, 77, 33).

The dehydration of Phenols or of Naphthols to give di-phenylic or di-naphthylic ethers is similar. Diphenyl ether, $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{C}_6\text{H}_5$, cannot be made by this reaction, but β -Naphthol and derivatives of β -Naphthol form $\beta\beta'$ -di-naphthylic ethers with ease. Thus, Graebe obtained the ether of β -Naphthol by boiling a mixture of β -Naphthol and 50 per cent. Sulphuric acid for some hours (*Ber.*, 1880, 13, 1850), and it is within the experience of the present author that β -Naphthol cannot be sulphonated at 100°C ., or higher for the formation of Schaffer acid or β -Naphthol disulphonic acid R without loss of β -Naphthol, due to formation of sulphonic acids of the ether, amounting to 10–20 per cent. of the β -Naphthol used.

Other acids besides those mentioned can be used as etherification catalysts. Thus, for the formation of Ethyl ether, either halogen acid at $200\text{--}240^\circ\text{C}$. is practicable (Reynoso, *Ann. Chim. Phys.*, 1856, (3), 48, 385); while for technical working Benzene sulphonic acid has been much favoured in place of Sulphuric, on account of its less tendency to char the Alcohol (Krafft, *Ber.*, 1893, 26, 2831; D.R.-P. 69115).

Preparation of Dimethyl Ether. The methods to be described for

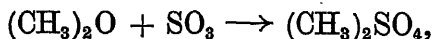
the formation of ordinary ether are equally satisfactory for the laboratory or technical production of Dimethyl ether. Thus, dehydration is rapid when Methyl alcohol is introduced below the surface of a catalysing acid, maintained at a suitable temperature in a retort, and the ether, water, and unchanged alcohol distil.

A more convenient method of preparation, which enables the rate of production to be increased almost to any desired scale, consists in passing Methyl alcohol vapour over a porous substance soaked in syrupy Phosphoric acid, and heated to a temperature not exceeding 270° C. Siliceous supports for the Phosphoric acid cannot be used, since at temperatures above 200° C. a solid Phosphosilicic acid is formed by action between the catalyst and the support, which is catalytically inert. Coke or other carbonaceous supports are satisfactory.

Granulated coke, soaked in Phosphoric acid, is heated to 200–300° C. in a slow current of air until all the liquid has disappeared, and then packed into an iron tube fitted with temperature registering and heating arrangements. The temperature is then raised to 230–260° C., and a swift current of Methyl alcohol vapour from a boiler passed. At a suitable space velocity the conversion is very high and the yield nearly quantitative. The product is purified from unchanged alcohol by water scrubbing, and the Dimethyl ether then liquefied by refrigeration or compression, or absorbed in strong Sulphuric acid, which dissolves many times its own volume.

Dehydrating oxide catalysts, preferably Alumina, precipitated from the nitrate by means of Ammonia and dried at 300° C. can also be employed for the production of Dimethyl ether in almost quantitative yield from Methyl alcohol, the reaction being carried out at a temperature of 250–350° C. as before, in an iron tube.

The chief use of Dimethyl ether is, for the preparation of Dimethyl sulphate, formed by direct union with Sulphur trioxide,



a reaction which takes place smoothly in Dimethyl sulphate solution at the ordinary temperature with generation of heat.

Manufacture of Ether. Till comparatively recently, the manufacture of Ether was carried out by a simple magnification to the works scale of the original laboratory method due to Boullay (*Gilbert's Ann.*, 1813, 44, 270; *J. Pharm. Chim.*, 1, 97).

Commercial Sulphuric acid (9 parts) and 90 per cent. Alcohol (5 parts) are mixed in a lead-lined Iron retort and heated to 130–145° C., the temperature at which the reaction must be carried out. While maintaining the temperature at this point (registered by means of a thermometer filled with air, Mercury, or a non-drying oil), Alcohol is added at a rate approximately equal to the rate of its

disappearance by dehydration to Ether and water. The heating is generally carried out by superheated steam or the vapour of a high boiling liquid, refluxing through leaden coils within the retort. The distillate, consisting of Ether and water, is purified by shaking with lime or soda to remove Sulphur dioxide (always formed in small quantities by reduction of the Sulphuric acid) and fractionally distilling.

Soubeiran's apparatus combines the processes of manufacture and purification in one operation. A mixture of 30 lb. of Sulphuric acid and 20 lb. of 85 per cent. Alcohol is quickly heated to 130° C. in a copper still. At this temperature, Alcohol is introduced at the bottom of the still through a tube dipping below the surface of the acid, at a rate which balances the disappearance of Alcohol by reaction. The vapours are conducted *via* a leaden neck to a copper condenser, maintained about the boiling point of Ether by water warmed by use in the Ether condenser. Here the water and Alcohol condense, the former almost completely, owing to the scrubbing action exercised by the condensation of the latter. The Ether vapour passes through a purifier containing wood charcoal impregnated with caustic Soda solution, to absorb Sulphur dioxide, and is then condensed.

Such processes as those just described were unable to cope with the increasing demand for Ether, being cumbersome, and slow in operation, and not very efficient either in the reaction or the rectification. Modern methods therefore bring the Alcohol vapour into intimate contact with the liquid catalysing acid at the temperature of reaction—viz. 140° C.—and fractionally condense the products in dephlegmating apparatus, which effects a sharp separation into water, condensing first, Alcohol, and, lastly, Ether. The reaction is exothermic, so that heat must be withdrawn during the reaction by cooling.

Barbier's still consists of a tower divided into sections—twelve at least—each containing heating coils, and plates or baffles, for dispersing liquid flowing down. Alcohol is introduced into the fourth section from the bottom, while commercial Sulphuric acid is fed in at the top, and, descending, is quickly raised by the coils to the reaction temperature. The Alcohol vapour in contact with the hot Sulphuric acid is rapidly dehydrated, and as it ascends, meeting stronger and stronger acid, is finally converted to the extent of 70 to 80 per cent. into water and Ether. Since the unchanged Alcohol is recovered in the dephlegmator, an overall yield of at least 95 per cent. of theory is easily attainable. In the three lowest sections of the tower, unchanged Alcohol and Ether are vaporised from the down-flowing diluted Sulphuric acid, which collects at the bottom and is concentrated for using again (see F.P. 479435 of 1914, E.P. 100406 of 1916, and U.S.P. 1328258). The same apparatus can be employed

for the manufacture of Ethyl acetate or other esters. The Ether obtained by this method is very pure, the chief impurities, water, Alcohol, Aldehyde, and Vinyl alcohol, tending to condense in either the water or Alcohol fractions.

Other acids besides Sulphuric may be used in this process—some of which have the advantage of inducing no bye-reactions, and therefore more easily give a pure product. In particular, Benzene sulphonic acid has been recommended by Krafft and Roos (D.R.-P. 69115), but it does not appear to have superseded Sulphuric acid, the use of which enables extremely efficient results to be obtained.

Apparatus applying similar principles is described in F.P. 408089, and by Fritzsche (*Z. anal. Chem.*, 1897, 36, 298).

Senderens has shown that the presence of Aluminium or Lead sulphates in the reaction mixture catalyses the dehydration of Alcohol by Sulphuric acid (*C.R.*, 1910, 151, 392). Thus, in the absence of one of these salts, the evolution of Ether does not become regular until a temperature of 140° is reached. In presence of 5 to 10 per cent. of Aluminium sulphate, on the other hand, this temperature of working can be advantageously lowered to 130° C. Schlatter (*J. Ind. Eng. Chem.*, 1920, 12, 1101) confirmed Senderens' observation, but found that in lead-lined apparatus any addition was unnecessary, the accidental presence of Lead sulphate serving the same purpose. Aluminium sulphate, in fact, caused considerable pitting of the lead lining.

The conditions of the reaction were also investigated by Prescott and Norton, who showed that in the absence of any promoter the optimum temperature for the dehydration of Alcohol by Sulphuric acid was 140–145° C., lower temperatures giving inferior yields, and higher temperatures leading to greater formation of Sulphur dioxide and Ethylene (*Amer. Chem. J.*, 1884, 6, 243).

Preparation of β -Naphthol Ethyl Ether. β -Naphthol (2 parts) and Ethyl alcohol (2 parts) are mixed with 1 part of concentrated Sulphuric acid and heated on a water-bath under a reflux condenser for 6 hours, with continuous shaking or stirring. The product while still warm is then run into a dish and allowed to cool, when the ether sets to a solid, crystalline crust at the top. When cold, this is pierced, the liquor beneath drained off, and the acid and excess of alcohol are recovered. The solid is first washed with cold water and then melted with dilute caustic Soda solution to extract unchanged β -Naphthol, after which it is again washed with warm water and allowed to solidify with agitation, when the pure ether is obtained as a granular mass. It can be completely purified by distillation.

For the preparation of α -Naphthol methyl ether, Krafft and Roos recommend the use of Naphthalene β -sulphonic acid as catalyst,

gradually running a hot solution of α -Naphthol in Methyl alcohol into the acid at 140–145° C. (D.R.-P. 76574 of 1893; E.P. 6190 of 1894).

Acid Anhydrides as Catalysts. These are more energetic dehydrants than the mineral acids, into which, however, they may pass by combination with the first equivalent of water extracted from the substances upon which they are reacting. Their action then becomes similar to that of the corresponding mineral acid.

For preparation of phenolic ethers, such as Anisole and Phenetole, a powerful dehydrant is necessary, mineral acids not, in general, sufficing, and Kastropp has described the formation of the latter compound by interaction between Phenol and Ethyl alcohol in presence of Phosphoric anhydride (*Ber.*, 1877, 10, 1685).

Acid anhydrides generally are too vigorous dehydrants to yield ethers from alcohols, and, except in the case of Methyl alcohol, which gives Dimethyl ether, dehydrate immediately to unsaturated hydrocarbons.

Anhydrous Chlorides as Catalysts. Many years ago, Masson showed that anhydrous Zinc chloride, heated with alcohol, dehydrated it to ether (*Lieb. Ann.*, 1839, 31, 63). Kuhlmann, shortly after, proved that Stannic chloride was able to effect the same reaction (*ibid.*, 1840, 33, 97, 192). Berthelot obtained Ether by heating alcohol to 260–400° C. in presence of dry Ammonium chloride (*Ann.*, 1852, 83, 110) and Reynoso still further extended the list of dehydrating anhydrous chlorides which catalysed the reaction to the chlorides of Tin, Zinc, Mercury, and Calcium (*Ann. Chim. Phys.*, 1856, (3), 48, 385). These substances are capable of general use as etherifying agents, but are not commonly used. Zinc chloride cannot be used with Methyl alcohol, since a complicated reaction leads to the formation of numerous gaseous products, while a small quantity of Hexamethyl benzene is stated to be formed (Le Bel and Greene, *C.R.*, 1878, 87, 260).

Inorganic Salts possessing an Affinity for Water, as Catalysts. Reynoso showed that Magnesium sulphate, and also Chrome alum at 300° C., dehydrated Alcohol to Ether (*Ann. Chim. Phys.*, 1856, (3), 48, 385). Mailhe and de Godon, guided by the observation that Aluminium sulphate facilitated the dehydration of Alcohol with Sulphuric acid, have applied calcined Alum to the preparation of ethers from alcohols generally (*Bull. Soc. chim.*, 1919, IV, 25, 565; 1920, IV, 27, 121, 328). The following reactions were carried out with the dried Alum at 160–200° C. It was found that water retarded the reaction. Methyl and Ethyl alcohols gave very high yields of the ethers, no Aldehyde or Ethylene being obtained from the latter. Dipropyl ether was obtained from Propyl alcohol at 185° C. A little Propylene was formed at the same time, but no Propionaldehyde. At 195° C., formation of Propylene became much more important.

isoPropyl alcohol in the same way gave isoPropyl ether at 150–160° C., but the tendency to dehydrate to Propylene was much more marked even at this low temperature. The higher alcohols also gave ethers with calcined Alum as catalyst, but generally in low yields. Thus from 50 c.c. of isoButyl alcohol, 2 c.c. of isoButyl ether, $[(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2]_2\text{O}$, were obtained. Normal Butyl alcohol (20 c.c.) gave, however, 4 c.c. of Butyl ether, while isoAmyl alcohol, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, though it gave much Amylene, gave a fair yield of ether with alum at 185° C.

Mixed ethers also were obtained in addition to the two simple ethers, when the vapours of two alcohols were mixed and led over calcined Alum, and when isoPropyl or isoButyl alcohols were used, the yield of mixed ether was often better than the yield of the simple ether obtained when either of these alcohols was used alone. Using approximately equimolecular proportions of the appropriate alcohols, notable proportions of the following mixed ethers were obtained, in addition to the corresponding simple ethers and olefines, by contact with calcined Alum at about 185° C. : Methyl-ethyl, Methyl-propyl, Methyl-isobutyl (more difficultly), Ethyl-isobutyl, Ethyl-isoamyl, Propyl-isoamyl, isoButyl-isoamyl, Methyl-isoamyl, Ethyl-propyl, Ethyl-butyl, Propyl-isobutyl. In all cases where Methyl alcohol was used, a large proportion of Dimethyl ether was formed.

Allyl alcohol also gave Diallyl ether, as well as mixed ethers, when passed alone, or with the vapour of a second alcohol over alum at 185–190° C. The yields of mixed ethers, using Allyl alcohol, were very good, the formation of simple ethers even when they ordinarily formed easily being checked by the presence of the more reactive Allyl alcohol. Thus, an equimolecular mixture of Methyl and Allyl alcohols gave a little Dimethyl and Diallyl ethers, with more Methyl allyl ether. Doubling the proportion of Methyl alcohol did not improve the yield of mixed ether. Ethyl and Allyl alcohols in equimolecular proportions gave a 7–8 per cent. yield of Allyl ethyl ether, which increased to 10 per cent. on doubling the proportion of Ethyl alcohol. Yields of mixed ethers from the higher alcohols and Allyl alcohol were lower, but were obtained in the following cases, in addition to the two simple ethers, and olefines:—Propyl-allyl, isoButyl-allyl, isoAmyl-allyl. No aldehyde or other dehydrogenation product was observed, but with isoButyl and isoAmyl alcohols higher condensation products were obtained.

Benzyl alcohol gave small amounts of the mixed ether with Methyl and Ethyl alcohols, but the tube soon became obstructed with the yellow, resinous dehydration product of Benzyl alcohol, $(\text{C}_7\text{H}_6)_n$, previously described by Sabatier and Mailhe (*Ann. Chim. Phys.*, 1910, (8), 20, 298).

Both primary and secondary alcohols, saturated and unsaturated,

and aromatic alcohols therefore yield ethers by contact with calcined Alum.

Phenolic ethers can be prepared by use of a dehydrating salt at a suitably high temperature in an autoclave. Thus, Anisole is made by heating Methyl alcohol and Phenol to 150–160° C. in presence of Potassium hydrogen sulphate (D.R.-P. 23775). The yields in such reactions, however, do not appear to be high, on account of the superior tendency for dehydration to take other courses—olefine formation—or, when Methyl alcohol is used, formation of Dimethyl ether.

Dehydrating oxides as Catalysts, (a) Dehydration of Alcohols. Alumina only, and at a low temperature (below 300° C.), is capable of yielding ethers from primary alcohols other than Methyl alcohol. Other catalysts, such as Thoria, Tungsten oxide, etc., give only the corresponding olefine, or effect dehydrogenation instead of dehydration. The Alumina must be precipitated, preferably from Sodium aluminate with the requisite quantity of mineral acid, and dried at a low temperature.

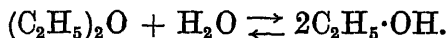
Alumina prepared in this way is the only dehydrating oxide that gives ether exclusively even from Methyl alcohol. The dehydration begins about 240° C., and becomes fast at 300° C. At 350° C., some dehydrogenation also sets in. Other dehydrating oxides also give ether from Methyl alcohol, but never quantitatively. Thus, among the best are Thoria, the blue oxide of Tungsten, and Chromic oxide, which, above 230° C., give mainly Dimethyl ether, and also some Formaldehyde, and decomposition products. Titania, while giving mainly ether, gives still more Formaldehyde. Other oxides, such as those of Zirconium, Molybdenum, and Vanadium, which, with higher alcohols, give considerable quantities of dehydration products (olefines), with Methyl alcohol give almost exclusively dehydrogenation (Formaldehyde) (Sabatier and Mailhe, *Ann. Chim.*, 1910, (8), 20, 345; Senderens, *Ann. Chim. Phys.*, 1912, (8), 25, 449).

The same active preparation of Alumina commences to give Diethyl ether from Ethyl alcohol about 190° C., but a little Ethylene is always formed, the quantity increasing as the temperature is raised. At 240–260° C., a high yield of very pure ether can be obtained from alcohol in contact with active Alumina. It is not necessary to use pure Alcohol, 90 per cent. rectified spirit giving equally good results (Senderens, *C.R.*, 1909, 148, 227, 927). Above 300° C., Alumina dehydrates Ether into Ethylene, so that at such temperatures Ethylene will always be the main product (Senderens, *C.R.*, 1908, 146, 1211; Engelder, *J. Phys. Chem.*, 1917, 21, 676).

Dipropyl ether can be made in the same way by the use of an Alumina catalyst, but the maximum yield is about 30 per cent., mostly Propylene being obtained.

isoButyl and the higher alcohols give only the corresponding olefine, even with Alumina at the lowest possible working temperature.

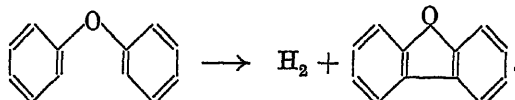
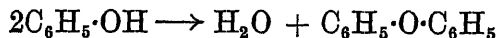
Under high pressure, the action of Alumina on Alcohol is similar, but the degree of reaction is limited by the reverse :



At high temperatures, as before, only Ethylene is formed (Ipatiev, *Ber.*, 1904, 37, 2961).

(b) *Dehydration of Phenols.* The decomposition of Aluminium phenolates, with formation of the corresponding phenolic ethers, was discovered by Gladstone and Tribe, in the cases of Phenol and the ortho- and para-Cresols (*J.C.S.*, 1882, 41, 9; 1886, 49, 29). Sabatier and Mailhe based on this observation a general catalytic method for the formation of phenolic ethers from phenols (*C.R.*, 1910, 151, 492). The vapour of the phenol was passed over a dehydrating oxide catalyst, best Thoria, heated to 390–450° C., the product condensed, unchanged phenol extracted by shaking with caustic alkali, and the ether obtained in a pure state from the remaining substance by fractional distillation.

Simultaneously with the formation of ether by dehydration, pyrogenous dehydrogenation partially occurs, more and more as the temperature is raised, with formation of phenylene oxides, by fusion of two benzene rings. Thus, with Phenol,



In this way ethers and phenylene oxides were made from Phenol, meta- and para-Cresols, Carvacrol, and 1:3:4-Xylenol. ortho-Cresol ether was also obtained, but its formation required a higher temperature, so that the yield was lower (*Bull. Soc. chim.*, 1912, (4), 11, 843). Naphthols behave similarly.

The phenylene oxides are fluorescent substances, less volatile than the corresponding ethers. Their formation during the dry distillation of Calcium phenolates had already been observed by Niederhausen (*Ber.*, 1882, 15, 1120).

Dehydration by Thoria can also be applied to a mixture of two phenols, when, in addition to the two simple ethers, a varying proportion of the mixed ethers results, together with the corresponding diphenylene oxides. In this way, Sabatier and Mailhe prepared the following mixed ethers: Phenyl ortho-cresyl, Phenyl meta-cresyl, Phenyl para-cresyl, Phenyl- α -naphthyl, Phenyl- β -naphthyl, para-Cresyl- α -naphthyl, and para-Cresyl- β -naphthyl. In each case,

simple ethers were also formed, as well as the mixed, together with the corresponding phenylene oxides (*C.R.*, 1912, 155, 260).

In the same way, a mixture of a phenol and an alcohol produces the corresponding mixed aliphatic phenolic ether (Sabatier and Mailhe, *C.R.*, 1910, 151, 359). A mixture of the vapours of the phenol and the alcohol, containing excess of the latter, is led over a dehydrating oxide, best Thoria at 390–420° C., and the resulting vapours are condensed. The mixed ether is then separated by fractional distillation after first extracting unchanged phenol by means of caustic alkali. Anisole is formed by this method in good yield from Phenol and Methyl alcohol, also the methyl ethers of the three Cresols, 1:2:4- and 1:3:4-Xylenols, Thymol, Carvacrol, and α - and β -Naphthols. Ethyl alcohol and the higher alcohols react similarly, but less satisfactorily on account of the greater readiness with which dehydration can take an alternative course, olefines being formed, which occurs very actively with Thoria at 420° C. Sabatier and Mailhe obtained, however, high yields (reckoned in the Phenol) of the Ethyl, Propyl, isoAmyl, etc., ethers of Phenol and para-Cresol, the reaction being most conveniently carried out by dissolving the phenol in excess of the alcohol and volatilising the solution over the heated catalyst. The simultaneous formation of the diphenylic ether and diphenylene oxide is generally small, by far the greater proportion of the phenol which undergoes change giving the mixed ether.

Ethers could not be obtained from dihydric phenols, owing to formation of stable compounds with the Thoria, these being slowly decomposed to give complex products.

In a more recent paper, Sabatier and Mailhe described the preparation of a number of ethers of Carvacrol (*C.R.*, 1914, 158, 608). Dehydration of Carvacrol alone, with Thoria at 400–500° C., gave a

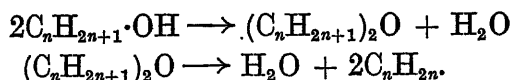
mixture of the ether, Dicarvacryl oxide, $\begin{array}{c} \text{C}_6\text{H}_5 \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{C}_3\text{H}_7 \end{array} \\ | \\ \text{O} \\ | \\ \text{C}_6\text{H}_5 \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{C}_3\text{H}_7 \end{array} \end{array}$, and Dicarvacrylene oxide, $\begin{array}{c} \text{C}_6\text{H}_5 \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{C}_3\text{H}_7 \end{array} \\ | \\ \text{O} \\ | \\ \text{C}_6\text{H}_5 \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{C}_3\text{H}_7 \end{array} \end{array}$, not separable by fractional distilla-

tion. Methyl alcohol and Carvacrol passed over Thoria at 420–450° C. gave mainly the methyl ether of Carvacrol, together with a little Dicarvacryl ether. At a higher temperature, the Dicarvacrylene oxide commenced to form. Ethyl alcohol and Carvacrol gave a much lower yield of the Ethyl ether, together with Dicarvacryl ether. An equimolecular mixture of Phenol and Carvacrol with Thoria at 470–480° C. gave Phenyl-carvacryl ether, together with

Dicarvacryl ether and Dicarvacrylene oxide, but no Diphenyl ether or Diphenylene oxide. para-Cresol, at 440–450° C., on the other hand, gave the Carvacryl para-tolyl ether and Di-para-tolyl ether, and no Dicarvacryl ether, while at 480° C., the mixture behaved like para-Cresol alone.

The Formation of Olefines

The complete dehydration of alcohols, whereby an olefinic hydrocarbon is produced, is facilitated by a very large number of catalytic agents, among which only those already mentioned enable the intermediate ether stage to be isolated. Ethers likewise are dehydrated to olefines,



Elementary Substances as Catalysts. Carbon, obtained from animal charcoal by washing with Hydrochloric acid, is a powerful catalyst for dehydration of alcohols, but the reaction is not clean, lower saturated hydrocarbons, oxides of Carbon, and Hydrogen being usual bye-products. These bye-products are probably produced by simultaneous dehydrogenation of the alcohol to aldehyde and Hydrogen, the former then undergoing decomposition into Carbon monoxide and a saturated hydrocarbon. It is possible that this action is largely due to mineral impurities in the catalyst, and that a much cleaner dehydration would be obtained with pure Carbon. In the case of Ethyl alcohol, Senderens found that this decomposition occurs to a considerable degree, at 350° C., giving a mixture of Ethylene, Methane, Carbon monoxide, and Hydrogen, the last three substances being formed by dehydrogenation, and decomposition (which may be only partial) of the aldehyde formed. Propyl alcohol, on the other hand, gave above 300° C. a gas consisting of 87 per cent. of Propylene, with small quantities of Ethane, Carbon monoxide, and Hydrogen (*C.R.*, 1907, 144, 381).

Phosphine can be made by passing steam over red Phosphorus at 240–250° C. If instead of water vapour an alcohol is used, very little Phosphine is formed, but mostly the olefine corresponding with the alcohol. Red Phosphorus is considerably more energetic in its dehydrating action than Carbon—inducing reaction at a much lower temperature—possibly owing to the presence of Phosphoric acid easily formed by oxidation. The utility of Phosphorus for this purpose is, however, much reduced on account of the formation of Phosphine, always produced to the extent of several per cent., which is difficult to remove from the hydrocarbon product.

Ethyl alcohol in contact with red Phosphorus commences to

decompose at 215° C. and at 230–240° C. rapidly gives a mixture of 95 per cent. Ethylene and 5 per cent. Phosphine. Propyl alcohol similarly gives Propylene. Dehydration is easier in the cases of Butyl and isoButyl alcohols, and easier still with isoPropyl alcohol, which reacts at 150° C. The formation of Phosphine is then correspondingly reduced. Thus, Butyl alcohol reacts rapidly at 205° C., giving 97 per cent. of Butylene and 3 per cent. of Phosphine, while the dehydration of isoPropyl alcohol at 150° C. is almost unaccompanied by formation of Phosphine (Senderens, *C.R.*, 1907, 144, 1109; *Bull. Soc. chim.*, 1907, (4), 1, 687).

Finely-divided metals, which dehydrogenate primary and secondary alcohols, are unable to effect this reaction with the tertiary, which, accordingly, are dehydrated instead, a reaction which they very readily undergo. Nickel at 220–300° C., or Copper at 280–300° C., dehydrates tertiary alcohols to olefines almost without bye-reactions (Sabatier and Senderens, *Ann. Chim. Phys.*, 1905, (8), 4, 467).

Sabatier and Senderens employed catalytic Copper at 300° C. to ascertain the constitution and purity of alcohols: the primary gave aldehydes, the secondary gave ketones, and the tertiary gave unsaturated hydrocarbons (*Bull. Soc. chim.*, 1905, (3), 33, 263).

Mineral Acids as Catalysts. The formation of ethers from alcohols when treated with a concentrated mineral acid occurs at comparatively low temperatures in the manner already shown. Except in the case of Methyl alcohol, however, ether formation is always accompanied with production of more or less olefine, and this reaction becomes more pronounced as the temperature is raised. Above about 180° C., or lower in many cases, the olefine is generally the exclusive product, and is formed from almost all alcohols, primary, secondary, or tertiary. Using Sulphuric acid, a certain amount of Sulphur dioxide is found in the product, and some carbonisation of the alcohol occurs. Phosphoric or Arsenic acid gives a pure product and no carbonisation.

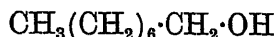
Ethyl alcohol, with Sulphuric acid, commences to give Ethylene just above 140° C., and gives it rapidly and nearly quantitatively at 180° C. (Erlenmeyer, *Ann.*, 1878, 192, 244). Normal Propyl, Butyl, and isoButyl alcohols similarly give respectively Propylene and Butylenes. isoPropyl alcohol commences to react at a lower temperature, also yielding Propylene.

Senderens has shown that fine quartz sand in the reaction mixture aids dehydration and functions as a true catalyst. Anhydrous Aluminium or Lead sulphates were shown to be still more effective when some 5 per cent. was dissolved in, or added to, the Sulphuric acid. With Alcohol at 157° C., the rate of evolution of Ethylene was thereby increased threefold. Propyl alcohol gave Propylene at 130° C. as readily as at 145° C. in the absence of the promoter, while

isoButyl alcohol commenced to decompose at 125° C. (*C.R.*, 1910, 151, 392).

Adams, Kamm, and Marvel prepared Amylene on a considerable scale as follows: 1500 c.c. of isoAmyl alcohol and 100 c.c. of strong Sulphuric acid were heated in a vessel under a reflux condenser maintained at 60–90° C. This returned the less volatile products to the still, while the Amylene (a mixture of three isomers) was condensed later in a well-cooled coil. 250 Grams of Amylene were made in 8 hours. The alcohol remaining in the still contained 400 grams of isoAmyl ether, showing (at variance with published statements to the contrary) that, under suitable conditions, the higher alcohols, like the lower, yield ethers when dehydrated with mineral acids (*J. Am. C.S.*, 1918, 40, 1950).

Senderens has investigated the dehydration of alcohols by means of Sulphuric acid in great detail (*C.R.*, 1912, 154, 777, 1168). The alcohols were in each case heated with 3 to 4 per cent. by volume of the concentrated acid. It was found that the olefine was more easily obtained from the higher members of the series, this being due to the temperature of reaction being more easily reached in the case of the higher alcohols, where the boiling points rise continuously with increasing complexity. At the same time, tertiary alcohols were found to dehydrate much more readily than secondary, and these more easily than primary. Thus, even the lowest of the tertiary alcohols was dehydrated to olefine. Among the secondary alcohols, only those above C_5 were attacked under the same conditions, and of the primary, only those above C_8 , as follows: $(CH_3)_3C \cdot OH$ and $(CH_3)_2(C_2H_5) \cdot C \cdot OH$ readily gave the corresponding ethylenic hydrocarbons, $\begin{matrix} C_3H_7 \\ CH_3 \end{matrix} > CH \cdot OH$ gave two isomeric pentenes, and $CH_3(CH_2)_5CH(CH_3) \cdot OH$ the two corresponding Octenes.



also gave Octene, and some of the dimeric compound. The following alcohols, however, were not dehydrated at all, or only to a very small extent, under the same conditions: isoPropyl, Ethyl, *n*-Propyl, isoButyl, and isoAmyl. Sabatier drew the same conclusion, already reached in connection with the dehydration to Ethers, that Sulphuric acid is a true catalyst, and like all catalysts requires a certain temperature to induce reaction. For the alcohols, this temperature rises in the order Tertiary, Secondary, Primary, and since it is more easily reached with the higher alcohols, these are the more convenient to dehydrate with small quantities of acid. For this reason, dehydration of Ethyl alcohol to Ethylene needs a large quantity of Sulphuric acid, the mixture otherwise boiling at a temperature too low for dehydration.

Cyclanols by heating with 3 to 4 per cent. by volume of Sulphuric acid are dehydrated to the corresponding cyclenes. With Cyclohexanol, an 89 per cent. yield of Cyclohexene is obtained by simple distillation of the mixture until white fumes, with the odour of Sulphur dioxide, commence to be evolved. The yield by the "dry method" of dehydration (Alumina or Thoria catalyst) is rather higher, but the process is not so convenient. The three Methyl cyclohexanols and 1:3:4-Dimethyl cyclohexanol similarly are dehydrated in high yield to the same products as are produced by the dry method, and Menthol, distilled with 1 to 2 per cent. of its volume of Sulphuric acid, gives a yield of Menthene equal to that obtained in the dry way. This yield is not diminished if 4 to 5 per cent. of Sulphuric acid, diluted with twice its volume of water, is used instead of the strong acid, confirming that the action of the acid is catalytic and does not depend upon its affinity for water. Potassium bisulphate and Boric acid likewise dehydrate Menthol in the "wet way," but less energetically than Sulphuric acid. Anhydrous Aluminium sulphate, however, gives only traces of Menthene.

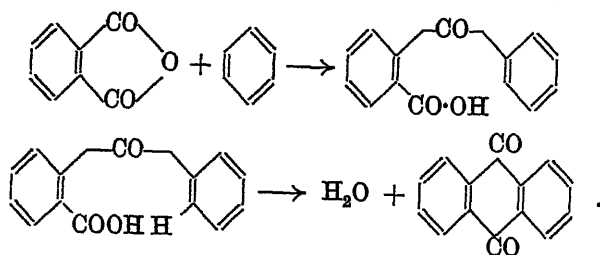
The Preparation of Ethylene from Alcohol by Dehydration with Mineral Acid. A mixture of concentrated Sulphuric acid (200 c.c.), 95 per cent. alcohol (100 c.c.), and dehydrated Alum (25 grams) is placed in a flask of suitable capacity, fitted with a thermometer dipping into the mixture, a dropping funnel, and a delivery tube, and heated to 160–185° C. Additional Alcohol is admitted by means of the dropping funnel below the surface of the mixture, at a rate roughly equal to its rate of disappearance by volatilisation and reaction. The Ethylene is evolved rapidly, and passes *via* the delivery tube to the purifying and collecting apparatus, such as will be described in greater detail in connection with the larger scale manufacture of Ethylene. Instead of Aluminium sulphate as a promoter, fine sand can be used to assist the evolution of Ethylene, this being preferable when lead-lined plant is used for the reaction, owing to some slight action of Aluminium sulphate on Lead.

When Ethylene is required in large quantities, dehydration of Alcohol in the vapour phase, and Phosphoric acid as the catalyst, are preferable, since a higher temperature can then be used and carbonisation at the same time avoided. Metallurgical coke is granulated to a convenient size and soaked in syrupy Phosphoric acid, thorough impregnation being assisted by heating and evacuation (siliceous supports are better avoided, owing to reaction between Phosphoric acid and Silica at a high temperature). The coke is then drained and heated to 200° C. in a current of air until it presents a dry appearance. It is then packed into an Iron, glass, or Silica tube, fitted with a movable pyrometer junction to record temper-

ature, and heated to 230–260° C. by any suitable means, preferably electrically. Alcohol vapour, from methylated spirit, is distilled from a boiler, and made to pass over the catalyst. Dehydration is extremely rapid and the yield of Ethylene high. It is purified by passing a series of cooled water scrubbers, in which the water and unchanged Alcohol are extracted from the gas, and on drying is sufficiently pure for chemical purposes, such as the manufacture of Ethylene chlorohydrin (reaction with water and chlorine, in presence of fine Calcium carbonate), or of $\beta\beta'$ -Dichloro diethyl sulphide—"Mustard gas" (by absorption in Sulphur chloride).

Acid Anhydrides as Catalysts. Anhydrides of the catalytically dehydrating inorganic acids, such as Phosphoric or Boric anhydride, can generally be used in place of the acids themselves to dehydrate hydroxy-bodies to ethylenic derivatives.

The elimination of water from an organic molecule by union between a hydroxy-group and a Hydrogen atom is a very common reaction in synthetic organic chemistry, and mineral acids or their anhydrides are the usual catalysts. This type of reaction is termed an "internal condensation," and consideration of such reactions must be deferred to a chapter dealing with the "Use of Condensing Agents." An internal condensation may lead to formation of an olefinic compound, or to ring closure, and examples of these types of reaction are exceedingly numerous. A single instance of each may be given here. When Diacetonyl alcohol, $(\text{CH}_3)_2\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$, is warmed with a few drops of strong Sulphuric acid and the mixture distilled, an almost quantitative yield of Mesityl oxide, $(\text{CH}_3)_2\text{C}:\text{CH}\cdot\text{CO}\cdot\text{CH}_3$, results (Kohn, *Monats.*, 1913, 34, 779). A general method for the preparation of Anthraquinone and its derivatives consists in heating ortho Benzoyl benzoic acid, or a derivative of this (made by condensation between a Benzene derivative and a derivative of Phthalic anhydride) with a condensing agent, generally Sulphuric acid or Sulphuric anhydride. The yield in these reactions is generally nearly quantitative,



The formation of lactones from γ -hydroxy-acids, of Pyrones from γ -diols, and the mutarotation of sugars and sugar alcohols, all catalysed by the presence of mineral acids, are similar reactions.

Use of Anhydrous Chlorides as Catalysts. The elimination of water from alcohols to form an unsaturated hydrocarbon can generally be effected by the use of an anhydrous chloride as catalyst, especially Zinc chloride. With Zinc chloride, it is usually convenient to use a sufficient quantity to combine with all the water eliminated to form a stable hydrate, so that in practice the catalytic function of the Zinc chloride fails to be recognised. When conditions are adjusted, however, so that a convenient working temperature is reached, then a small quantity of Zinc chloride effects the dehydration of unlimited quantities of alcohols. This may be realised by working under pressure, or by using a high-boiling alcohol, such as Cyclohexanol. When this is distilled in the presence of a little Zinc chloride, water is continuously distilled away with the Cyclohexene formed, and an almost theoretical yield of this latter compound obtained.

Many analogous reactions, which we have classed as "Condensations," also can be brought about by Zinc chloride, as well as by other anhydrous chlorides, especially those of Aluminium and Iron.

Ipatiev and Sdzitowecy (*Ber.*, 1907, 40, 1827) dehydrated the Butyl alcohols, and showed that different Butylenes were obtained according to the catalyst used. In contact with heated Alumina, isoButyl alcohol gave only isoButylene, identical with that obtained by dehydration of Trimethyl carbinol. When, however, isoButyl alcohol was passed through a Copper tube containing heated Zinc chloride, a mixture of the three Butylenes was formed. This did not appear to be due to isomerisation of isoButylene first formed, since it was shown that the Butylenes do not undergo such a change when subjected to the same conditions.

Secondary Butyl alcohol, passed through a Copper tube containing Alumina at 450°, gave β -Butylene and only traces of isoButylene. Over Zinc chloride at the same temperature, however, β -Butylene, together with considerable quantities of isoButylene, Methyl ethyl ketone, and a liquid unsaturated hydrocarbon were formed. The hypothesis advanced to explain these results supposed that the preliminary dehydration in contact with Zinc chloride resulted in the transient formation of a Cyclopropane derivative,

$$\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{CH} \cdot \text{CH}_3$$
 , which then isomerised.

Inorganic Salts possessing an Affinity for Water as Catalysts. Senderens classified the inorganic salts possessing dehydrating properties according to their activity towards Ethyl alcohol (*Ann. Chim. Phys.*, 1912, VIII, 25, 449). Those of highest activity commenced to dehydrate Alcohol at 250–270° C., and at 340° C. furnished pure Ethylene at the rate of 60–90 c.c. per minute per standard volume of catalyst space. In this group were Aluminium silicate, "modelling clay," anhydrous Aluminium sulphate, and

precipitated Alumina. Catalysts of medium activity commenced their action at 320–340° C., and, under comparable conditions with the foregoing, yielded 2–9 c.c. of Ethylene per minute. Such substances were the acid and neutral phosphates of Calcium and the acid phosphates of Magnesium and Aluminium. Catalysts of intermediate activity between these groups were precipitated Silica, and Magnesium pyrophosphate.

The dehydrating powers of hydrated Aluminium silicate, and of graphite, towards alcohols had already been noted by Ipatiev (*Ber.*, 1903, 36, 1990). Bouveault, using a vertical tube 1 metre long, dried the hydrated Aluminium silicate into 1 cm. cubes at 300° C. in a current of air, and then, using this apparatus at 300° C., dehydrated Alcohol at the rate of 1 kilo per day. Ethyl, Propyl, and isoButyl alcohols and Cyclohexanol all gave high yields of olefine, and were dehydrated rapidly. isoAmyl alcohol of fermentation gave two isomeric Amylenes, as when Zinc chloride or Alumina were used (*Bull. Soc. chim.*, 1908, (4), 3, 117). Senderens showed that with Aluminium silicate at 345–350° C., three Amylenes were formed, viz. β -Methyl Δ^{β} -butene, β -Methyl Δ^{α} -butene, and γ -Methyl Δ^{α} -butene. When the product was collected in three fractions, he obtained the following relative proportions by volume, respectively, of the three products: 1st fraction, 704 : 180 : 25; 2nd fraction, 595 : 238 : 65; 3rd fraction, 302 : 392 : 182. Hence, as the catalyst ages its action alters. Senderens supposed that the β -Methyl Δ^{β} -butene was formed by isomerisation of β -Methyl Δ^{α} -butene under the influence of the catalyst, and that the activity of the catalyst for this reaction diminished as the catalyst aged (*C.R.*, 1920, 171, 916).

Results obtained by Bouveault also indicated that all basic salts of Aluminium could serve as dehydrating catalysts. Many such have been used, and have given excellent results, especially the basic sulphate made by calcining Aluminium sulphate at a red heat (Sabatier and Mailhe, *Ann. Chim. Phys.*, 1910, (8), 20, 300).

Calcium sulphate made by dehydrating gypsum is a fair catalyst, commencing to attack alcohol at 370° C., and at 420° C. rapidly producing Ethylene with 6 per cent. of Hydrogen. Made at a red heat, Calcium sulphate is less active, and dehydration is rapid only at 460° C., when the Ethylene formed contains much more Hydrogen (Senderens, *Bull. Soc. chim.*, 1908, (4), 3, 633). Aluminium silicate, certain clays, and kaolin, on the other hand, are far more active at 420° C., and are not affected by calcination, while the Ethylene formed still contains only 6 per cent. of other gases.

Senderens has especially recommended Aluminium phosphate, which, it is suggested, combines the effects of Alumina and Phosphoric anhydride (*Bull. Soc. chim.*, 1907, (4), 1, 687; *C.R.*, 1907,

144, 1109). It is the most active of the various metallic phosphates, many of which (e.g., those of Nickel, Magnesium, and Calcium) exert a dehydrating action, and is suitable for use generally in making either open-chain or cyclo-olefines. Ethyl alcohol commences to yield Ethylene at 330° C., and gives the pure gas abundantly at 380° C. *n*-Propyl alcohol commences to decompose at 300° C., and gives pure Propylene and water very rapidly at 340° C. *n*-Butyl alcohol at 320° C. rapidly dehydrates to a mixture of 27 per cent. isoButylene and 73 per cent. α -Butylene. isoButyl alcohol at 310° C. similarly gives a mixture of 68.5 per cent. of isoButylene and 31.5 per cent. of α -Butylene, while Trimethyl carbinol, like all tertiary alcohols, reacting at a much lower temperature, commences to give pure isoButylene at 140° C., and yields this hydrocarbon rapidly at 200° C.

Secondary alcohols again come between the primary and tertiary in regard to ease of dehydration. isoPropyl alcohol commences to give pure Propylene at 250° C., and rapidly at 300° C., while the catalyst is especially applicable for use with the cyclohexanols, Cyclohexanol itself; the three Methyl cyclohexanols, 1:3:4-Dimethyl cyclohexanol, and Menthol, all giving theoretical yields of the corresponding cyclo-olefines. Similarly, isoAmyl alcohol of fermentation, which dehydrates above 300° C., gives a mixture of α -isoAmylene (isoPropyl ethylene, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}:\text{CH}_2$) and γ -isoAmylene (Methyl ethyl ethylene, $(\text{CH}_3)(\text{C}_2\text{H}_5)\text{C}:\text{CH}_2$), with a little each of Trimethyl ethylene and 1-Pentene, while tertiary Amyl alcohol gives easily pure Trimethyl ethylene. Normal Octyl alcohol gives α -Octylene.

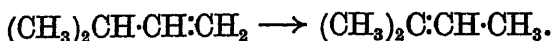
Silicates also were found to be strong dehydrating catalysts, but less so than the phosphates; while Silica itself, which is a strong dehydrant in the amorphous form, when crystalline is dehydrogenating.

Organic Acids, and Salts of Organic Acids as Catalysts. Condensation reactions can be frequently brought about between hydroxy and other compounds by heating with organic acids or salts, such as anhydrous Oxalic acid, Sodium acetate, etc. Such reactions may be considered in connection with "Condensation."

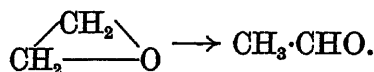
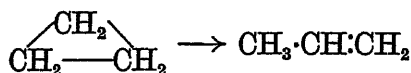
Dehydrating Oxides as Catalysts. The dehydrating power of certain oxides was first observed by Gregoriev, in the case of Ethyl and Propyl alcohols using Alumina (*J. Russ. Phys. Chem. Soc.*, 1901, 33, 173), which, at 300° C., was shown to give 90 per cent. yields of the corresponding olefines.

Ipatiev, as we have seen, discriminated between the two types of reaction which alcohols undergo, viz., dehydration and dehydrogenation, and showed that oxides were capable of facilitating either of these reactions, or, more often, both together. A catalytic method

for preparing Ethylene was first described in *Ber.*, 1903, 36, 1990, using as catalyst graphite, Silica, or china clay, or, best of all, Alumina at 350° C., when 98 per cent. of the Alcohol gave Ethylene and water. The similar decomposition of Propyl, isoPropyl, Butyl, isoButyl, and Amyl alcohols was also noted, as well as the isomerisation that certain of the olefines undergo in contact with Alumina at a high temperature. For example, α -isoAmylene was not changed by passage of its vapour through a glass tube heated to 500–550° C., but in contact with Alumina at the same temperature 80 per cent. was converted into Trimethyl ethylene,



isoButylene was shown not to undergo any similar change, so that the dehydration of isoButyl alcohol, which gives a mixture of isoButylenes, must follow an abnormal course. Trimethylene also was partially isomerised to Propylene, while Ethylene oxide and its homologues were isomerised to aldehydes or ketones (*Ber.*, 1903, 36, 2016),



Thus, Alumina at 200° C. converts Ethylene oxide into Acetaldehyde,

Propylene oxide, $\begin{array}{c} \text{CH}(\text{CH}_3) \\ \diagup \quad \diagdown \\ \text{CH}_2 \text{---} \text{O} \end{array}$, into Propylaldehyde and a little

Acetone, isoButyl oxide into isoButylaldehyde, and Trimethyl ethylene oxide into Methyl isopropyl ketone. Methyl ethyl ethylene

oxide, $\begin{array}{c} \text{C}(\text{CH}_3)(\text{C}_2\text{H}_5) \\ \diagup \quad \diagdown \\ \text{CH}_2 \text{---} \text{O} \end{array}$, similarly gives Methyl ethyl acetaldehyde.

A searching investigation of the catalytic effects of oxides on alcohols was carried out by Sabatier and Mailhe (*Bull. Soc. chim.*, 1907, (4), 1, 107, 341, 524, 773; *C.R.*, 1908, 146, 1376; 1909, 147, 16, 106; 148, 1734; *Ann. Chim. Phys.*, 1910, (8), 20, 289). These investigators showed that most oxides catalysed simultaneously both the dehydration and dehydrogenation of alcohols, but the relative degrees with which these reactions were augmented varied widely with different oxides. Some few oxides, when prepared in a special way, were found to be almost exclusively either dehydrogenating or dehydrating; the one type of reaction only being increased. Working with Ethyl alcohol, and various oxides maintained uniformly at 340–350° C., Sabatier and Mailhe estimated the relative dehydrogenating and dehydrating activities of a number of

oxides by measuring the volume of gas produced and determining the proportions of Hydrogen and Ethylene, respectively, contained. In this way they compiled the following catalytic classification of the chief non-reducible oxides. For comparison, all were made by precipitation and drying at a low temperature.

| Oxides. | Volume of gas produced per minute (c.c.). | Composition of the gas formed. | |
|--|---|--------------------------------|-----------------------|
| | | Hydrogen (per cent.). | Ethylene (per cent.). |
| Dehydrating oxides. | | | |
| Thoria, ThO_2 | 31 | traces | 100 |
| Alumina, Al_2O_3 | 21 | 1.5 | 98.5 |
| Blue oxide of Tungsten, W_2O_5 | 57 | 1.5 | 98.5 |
| Mixed Dehydrating and Dehydrogenating oxides. | | | |
| Chromic, Cr_2O_3 | 4.2 | 9 | 91 |
| Silica, SiO_2 | 0.9 | 16 | 84 |
| Titania, TiO_2 | 7.0 | 37 | 63 |
| Glucina, GhO | 1.0 | 55 | 45 |
| Zirconia, ZrO_2 | 1.0 | 55 | 45 |
| Urania, UO_2 | 14.0 | 76 | 24 |
| Molybdenum pentoxide, Mo_2O_5 | 5.0 | 77 | 23 |
| Ferric, Fe_2O_3 | 32.0 | 86 | 14 |
| Vanadious, V_2O_3 | 14.0 | 91 | 9 |
| Zinc, ZnO | 6.0 | 95 | 5 |
| Dehydrogenating oxides. | | | |
| Manganous, MnO | 3.5 | 100 | 0 |
| Magnesia, MgO | very little. | 100 | 0 |

The order implied by this table is, however, somewhat arbitrary. Thus, with other alcohols the order is quite different, and the nature as well as the degree of activity of the oxides vary greatly according to their mode of preparation. Amorphous forms are always more active than granular or crystalline forms of the same oxide. The most active oxide is therefore generally formed by precipitation and low temperature desiccation. Some oxides, though not all, are spoilt by drying at a high temperature. An extreme instance showing the arbitrary nature of this classification is Silica, which, in the amorphous form, prepared by precipitation, and drying at a low temperature, is almost exclusively dehydrating. Ignition of this Silica raises the relative amount of dehydrogenation it induces, and at the same time a much higher temperature becomes necessary for the catalyst to function, while crystalline mineral Silica, which requires a very high temperature, is nearly exclusively dehydrogenating. In all probability, a lower relative dehydrating activity is really responsible for the apparent increase in dehydrogenating properties (Senderens, *C.R.*, 1908, 146, 125; *Bull. Soc. chim.*, 1908, (4), 3, 823). Similar

differences, depending upon mode of preparation of the catalyst, its heat treatment, and the temperature of reaction, are observed with the other oxides also, especially Alumina and Chromic oxide, these facts doubtless explaining the different order given by Ipatiev, who arranged them as follows: Chromic oxide, Manganese oxide, oxides of Iron, Cobalt, Nickel, Copper, Zinc, the former yielding in the catalytic decomposition of Ethyl alcohol the least Aldehyde, and Zinc oxide the most. Oxides were also indicated as effecting similar catalytic actions to the corresponding metals, even though reduction did not appear to occur (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 508).

The table indicates that the most valuable dehydrating oxide catalysts are Thoria, Alumina, and Tungsten oxide. Alumina is most active when prepared by precipitation from the nitrate with Ammonia, well washing, and drying below 300° C., when it is in a very light porous form, easily soluble in acids. Crystalline or calcined Alumina is much less active, and dissolves only slowly in acids. This parallelism between the catalytic power of Alumina and its ease of solution in acids was also observed by Ipatiev (*Ber.*, 1904, 37, 2986).

Thoria also should be prepared by precipitation, in spite of the fact that a very light bulky form can be obtained by rapid decomposition of the nitrate. This form is comparatively inert. The precipitated oxide, unlike Alumina, can be calcined without losing its activity, and therefore possesses the advantage of being easily revived when deposition of carbonaceous matter has impaired its activity.

Tungstic oxide, WO_3 , is easily reduced by Alcohol vapour above 250° C., forming a blue oxide intermediate in composition between WO_3 and WO_2 , approximately represented by W_2O_5 . In air, this oxide tends to reoxidise to the yellow WO_3 . As a dehydrator, this blue oxide is very regular and active in the case of all alcohols except Methyl alcohol, giving a high yield of olefine. Methyl alcohol is simultaneously dehydrogenated to Formaldehyde and dehydrated to Dimethyl ether.

Chromic oxide and Silica, besides being less specific dehydrators, are much less active catalysts than the three already mentioned. As in the case of Alumina, this activity is much diminished by heating. For example, by passing Alcohol vapour over Chromic oxide at 350° C., which had not previously been heated above the temperature of reaction, Sabatier and Mailhe obtained 4.2 c.c. of gas per minute, containing 91 per cent. of Ethylene. Calcination much diminished this activity, and lowered the dehydrating action much more conspicuously than the dehydrogenating, so that after heating at 500° C., the same oxide gave only 2.8 c.c. of gas per minute, containing 40 per cent. of Ethylene. Oxide prepared by

rapid decomposition of Ammonium bichromate was less active still, the dehydrating action especially being reduced, the same quantity of catalyst in this case giving only 1.2 c.c. of gas per minute, containing 38 per cent. of Ethylene. Granular Chromic oxide has no action at all at 350° C., and at 400° C. gives only about 2 c.c. per minute of gas, chiefly Hydrogen. The dehydrating action has therefore been almost completely suppressed (Sabatier and Mailhe, *Ann. Chim. Phys.*, 1910, (8), 20, 339).

The life of dehydrating catalysts is affected mainly by two factors—the tendency for foreign material to be deposited during the course of the reaction and the liability of the catalyst to lose vigour by prolonged exposure to the reaction temperature. In most dehydration reactions decomposition products are gradually deposited upon the catalyst, reducing its activity, while Alumina appears gradually to diminish in activity with use, due, probably, to some change of physical form. Hence the particular advantages of Thoria, which is equally active after calcination, and therefore retains its activity for a long time, and, when devitalised by deposition of carbonaceous matter, can be restored completely by burning away the deposit. The blue oxide of Tungsten retains its activity longer than Alumina, but not so long as Thoria.

Increasing temperature much augments the speed of reaction, but at the same time, with the best dehydrating catalysts, likewise increases the tendency to dehydrogenate. Using a certain amount of Tungsten oxide, Sabatier and Mailhe found that it commenced to dehydrate Ethyl alcohol at 250° C., and that the rate of reaction then increased, as indicated by the figures :

| | | | | | | | | | |
|---------|---|---|------|-----------------------------|---|---|---|---|---|
| 260° C. | . | . | 5 | c.c. of Ethylene per minute | | | | | |
| 300 | . | . | 17.5 | " " | " | " | " | " | " |
| 310 | . | . | 27.0 | " " | " | " | " | " | " |
| 330 | . | . | 48.5 | " " | " | " | " | " | " |
| 340 | . | . | 57.5 | " " | " | " | " | " | " |
| 370 | . | . | 73.0 | " " | " | " | " | " | " |

(*Ann. Chim. Phys.*, 1910, (8), 20, 328).

Ipatiev has shown that increasing pressure retards the dehydration of alcohols, from which it would appear that the reaction is reversible (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 786, 813; 1906, 38, 63, 92).

The higher alcohols, from Butyl alcohol onwards, when subjected to catalytic dehydration, more especially in presence of oxides, generally give a mixture of the corresponding isomeric olefines, as well as polymerised products.

Dehydration of Methyl alcohol commences at 250° C. in presence

of Alumina (Thoria or the blue oxide of Tungsten is a less satisfactory catalyst with Methyl alcohol), is rapid at 300° C., and gives only Dimethyl ether. At 350° C., a small amount of Formaldehyde is produced, which may partially condense with the Methyl alcohol to Formal, or undergo decomposition to Carbon monoxide and Hydrogen.

Ethyl alcohol with Alumina at 240° C. gives almost exclusively Ether. Above 290° C., with Alumina, Thoria, or Tungsten oxide, pure Ethylene is produced, the reaction attaining its optimum at about 340° C. Propyl alcohol similarly with Thoria or Alumina gives Propylene at 300° C. without any trace of the ether. isoPropyl alcohol with Thoria at 260° C. likewise gives Propylene. Butyl, isoButyl, and isoAmyl alcohols at 320° C., with Alumina, Thoria, or Tungsten oxide give in each case a mixture of isomeric olefines, C_4H_8 or C_5H_{10} (Senderens, *Bull. Soc. chim.*, 1907, (4), 1, 692). Ipatiev and Sdzitowecy, however, obtained pure isoButylene from isoButyl alcohol and from tertiary Butyl alcohol (Trimethyl carbinol), and pure Butylene from secondary Butyl alcohol, with Alumina at 450° C. (*Ber.*, 1907, 40, 1827). Benzyl alcohol above 300° C. with Alumina or Tungsten oxide dehydrates readily, giving a polymer (C_7H_{8n}) without any evolution of gas (Sabatier and Mailhe, *Ann. Chim. Phys.*, 1910, (8), 20, 298).

Cyclic alcohols are similarly dehydrated, with formation in good yields of cyclenes. Thus, with Alumina, Cyclohexene is easily formed from Cyclohexanol, and Menthene from Borneol. Similarly, working under a pressure of 30–40 atmospheres in presence of Alumina at 350° C., Ipatiev obtained Dihydrobenzene, C_6H_8 , and a little tetrahydro phenol, C_6H_9OH , from Hexahydro hydroquinone, $C_6H_{10}(OH)_2$; and Octahydronaphthalene, $C_{10}H_{18}$, from Decahydronaphthol (*Ber.*, 1910, 43, 3383; *J. Russ. Phys. Chem. Soc.*, 1911, 42, 1552).

Unsaturated alcohols can be dehydrated in the same way, giving diethylenic hydrocarbons. Thus, Allyl alcohol at low redness was shown by Krestinski and Nikitin to give a certain amount of Propene, with more or less Acrolein (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 471), and Prévost has found that when the vapour of Ethyl vinyl carbinol, $CH_3 \cdot CH_2 \cdot CHOH \cdot CH : CH_2$, is passed over Alumina at 350–365° C., freshly prepared by precipitation from an aluminate by the action of Carbon dioxide, a 65 per cent. yield of 1 : 3-Pentadiene, $CH_3 \cdot CH : CH \cdot CH : CH_2$, is produced. Propyl vinyl carbinol, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CHOH \cdot CH : CH_2$, and Butyl vinyl carbinol were similarly dehydrated to the corresponding 1 : 3-Hexadiene and 1 : 3-Heptadiene (*C.R.*, 1926, 182, 853).

Manufacture of Ethylene by Catalytic Dehydration of Alcohol in the Dry Way. Large scale experimental plant, employing Mailhe's

process for the manufacture of Ethylene, has been described by Sprent (*J. Soc. Chem. Ind.*, 1913, 32, 171). The activity of the catalyst varied considerably according to its mode of preparation and physical form, amorphous forms giving a good yield of Ethylene while crystalline specimens did not. Many samples of Alumina gave no Ethylene at all, but converted the Alcohol into an oily substance. A rough indication of the usefulness of a specimen could be obtained by shaking with distilled water, when satisfactory forms always passed partially into colloidal solution, the particles of which moved towards the cathode when a current of electricity was passed. Catalytically inactive Alumina always sank immediately to the bottom. Kahlbaum's oxide "gereinigt" was especially recommended. The catalyst was contained in Iron tubes, 3 inches diameter and 5 feet long, connected at one end with the methylated spirit vaporiser, and at the other with purifying apparatus. The temperature was regulated at 360°C ., within narrow limits, the dehydration to Ethylene at this point being a maximum. At higher temperatures, the Ethylene began to decompose, giving Hydrogen, Methane, and Carbon, while the catalyst became gradually less efficient on account of the amorphous oxide slowly changing to crystalline, the change in nature of the catalyst reducing its activity, and in some degree leading to dehydrogenation. On the other hand, below 360°C ., the rate of reaction decreased and Ether commenced to be formed in increasing quantities. The Ether dehydration was at a maximum at 230°C ., and at 300°C . the Ether itself commenced to decompose to Ethylene and water. Below 360°C . there was always a probability of some Ether remaining undecomposed.

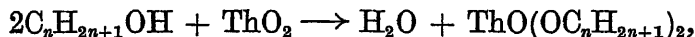
During the war large quantities of Ethylene were made for the manufacture of "Mustard gas" (Dichloro diethyl sulphide, $(\text{ClC}_2\text{H}_4)_2\text{S}$), and the above method with minor variations was generally adopted. The catalyst was usually Phosphoric acid, or Alumina in one of its naturally occurring, hydrated forms. Kaolin, in which Alumina is partially combined as Aluminium silicate, does not lose activity after long use at temperatures of 400°C .

Action of Dehydrating Catalysts on Polyhydric Alcohols. Dehydration of polyhydric alcohols does not lead to formation of diolefinic hydrocarbons, or, in fact, to hydrocarbons at all, the products usually being aldehydes and ketones. Thus, in presence of Alumina, Glycol, $\text{CH}_2\text{OH}\cdot\text{CH}_2\text{OH}$, at $420\text{--}480^{\circ}\text{C}$. gives Acetaldehyde, which partially condenses to Paraldehyde. Pinacone, $(\text{CH}_3)_2\text{C}\cdot\text{OH}\cdot\text{C}\cdot\text{OH}(\text{CH}_3)_2$, at $300\text{--}320^{\circ}\text{C}$. gives Pinacoline in the same way as under the action of dilute mineral acids (Ipatiev, *J. Russ. Phys. Chem. Soc.*, 1906, 38, 92). Glycerine is dehydrated to Acrolein, an action which is also brought about by other dehydrating agents, such as Aluminium sulphate or Potassium bisulphate. These act

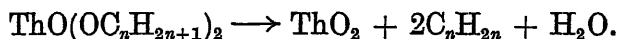
catalytically, and the large quantities usually recommended for the dehydration of Glycerine are not necessary. Thus, by heating 250 grams of Glycerine with 10 grams of Potassium bisulphate to 110° C. for 3 hours 130–140 c.c. of a liquid condensate are obtained, which, on redistillation, produce 34 to 38 c.c. of Acraldehyde. This yield is somewhat lower than that obtained by the more usual process, but the product is more stable, and polymerises comparatively slowly (Senderens, *Bull. Soc. chim.*, 1908, (4), 3, 828; *C.R.*, 1910, 151, 530). The sulphates of Iron, Copper, or Magnesium similarly dehydrate Glycerine (Wohl and Mylo, *Ber.*, 1912, 45, 2046).

Formation of Amines by Dehydration

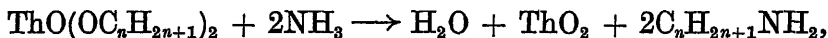
Sabatier's conception of catalytic dehydration by oxides involves a combination between the catalysing oxide and the alcohol (or phenol), giving transitorily the metallic salt of the hydroxy-body. For example, using an alcohol, and Thoria as catalyst,



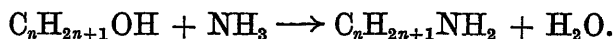
followed by



If this correctly represents the action of dehydrating oxides on alcohols, then, in presence of Ammonia, Sabatier and Mailhe supposed that the second stage of the reaction would more probably be



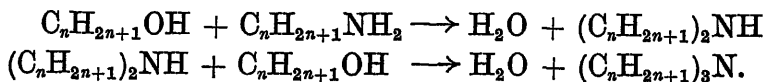
that is, when a hydroxy-body is passed with Ammonia over a dehydrating catalyst, the corresponding amines should be formed,



This anticipation was realised. Alcohol and Ammonia alone, at a high temperature, did not react, but in presence of Thoria at 300–350° C., amines were readily formed, almost without accessory formation of olefines, which the presence of Ammonia nearly completely inhibited.

Any of the dehydrating catalysts can be used: Alumina, Thoria, Tungsten oxide, Titania, Zirconia, Chromic oxide, or the blue oxide of Molybdenum (Mo_2O_5). In each case, the presence of the Ammonia stops not only the decomposition of the alcohol to olefine, but also its dehydrogenation to aldehyde.

In the case of all alcohols, the primary amine first formed reacts (like Ammonia) with unchanged alcohol, and gives secondary and tertiary amines,



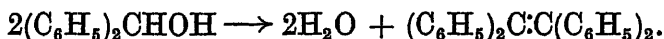
Frequently the rate of reaction between primary amine and alcohol is greater than that between Ammonia and alcohol, so that, under all conditions of concentration in the original mixture, secondary amine is formed in large quantity, and sometimes preponderates in the product. Tertiary amine is usually not formed so freely.

The method is quite general, and is brought about by passing the vapour of the alcohol, mixed with excess of Ammonia gas, over the heated catalyst and absorbing or condensing the products. Thoria at 250–350° C. is the best catalyst, since its period of activity is long, and revivification can be effected, when necessary, by ignition. In the case of all amines except the Methylamines, the primary, secondary, and smaller quantities of tertiary amines obtained can be readily separated from one another, and from unchanged alcohol, by fractional distillation. The statement by Hofmann that the three Ethylamines cannot easily be separated by distillation is erroneous.

The preparation of the primary, secondary, and tertiary amines corresponding with the simple aliphatic alcohols (Methyl, Ethyl, Propyl, isoPropyl, Butyl, isoButyl, Amyl, and isoAmyl) is described by Sabatier and Mailhe in *C.R.*, 1909, 148, 898; 1910, 150, 823, and especially in 1911, 153, 1204. In each case, at a suitable temperature, the reaction occurs without any complication. Benzyl alcohol and Ammonia, in presence of Thoria, give the three Benzylamines. The primary amine predominates if the temperature of the catalyst is about 330° C., while Dibenzylamine is the chief product at 370–380° C., but at such a temperature dehydrogenation to Benzaldehyde becomes marked, with some further decomposition to Benzene and Carbon monoxide (Sabatier and Mailhe, *C.R.*, 1911, 153, 160). The resinous dehydration product, $(C_7H_8)_n$, formed in very small amount, is gradually deposited upon the catalyst, and renders ignition necessary at intervals.

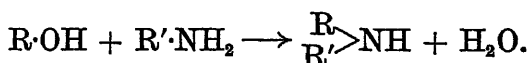
The secondary alcohols give a relatively greater formation of unsaturated hydrocarbon than the primary; a bye-reaction which can, however, be almost eliminated by working at a low temperature and accepting a comparatively low conversion—the hydrocarbon formation not commencing until a considerably higher temperature is reached than suffices for a fair rate of formation of amine. Thus, isoPropyl alcohol, with Ammonia, and Thoria at 250° C., gives a 20 per cent. yield of isoPropylamine, with a little secondary amine, but no bye-reactions, while at higher temperatures the two amines, together with much Propylene, result. Benzhydrol, $(C_6H_5)_2CHOH$, reacts with Ammonia with difficulty in presence of Thoria at 280° C. The amine is obtained, but the main product is Tetraphenyl ethylene, formed by dehydration in another way. This substance is obtained

in a high yield by heating Benzhydrol alone in presence of Thoria at 300° C.,



Cyclohexanol and its three methyl derivatives, which in contact alone with Thoria at 300–350° C. easily dehydrate to the corresponding Cyclohexenes, in presence of Ammonia react at 290–320° C., and for the most part give the primary and secondary amines, formation of the unsaturated hydrocarbon being hardly appreciable at this temperature.

In reacting with an alcohol, a primary aliphatic amine can be used, in place of Ammonia, when the product is a mixed secondary amine,



This reaction is brought about by passing an equimolecular mixture of the vapours of the alcohol and amine over Thoria at 320° C. Excellent yields of secondary amine are obtained with all alcohols, aliphatic, aromatic, and cyclic. Among the aliphatic, Methyl alcohol gives the least satisfactory results. Sabatier and Mailhe prepared from the substances indicated the following secondary amines (*C.R.*, 1909, 148, 900; 1911, 153, 1204): Ethyl isoamyl (Ethyl alcohol and isoAmylamine), Propyl isoamyl (Propyl alcohol and isoAmylamine), isoButyl isoamyl (isoButyl alcohol and isoAmylamine), Ethyl cyclohexyl (Ethyl alcohol and Cyclohexylamine), Propyl cyclohexyl (Propyl alcohol and Cyclohexylamine), isoButyl cyclohexyl (isoButyl alcohol and Cyclohexylamine), isoAmyl cyclohexyl (isoAmyl alcohol and Cyclohexylamine), Benzyl cyclohexyl (Benzyl alcohol and Cyclohexylamine); the 2-Methyl, 3-Methyl and 4-Methyl cyclohexyl cyclohexylamines (from 2-, 3-, and 4-Cyclohexanols and Cyclohexylamine); and Methyl cyclohexyl (from Methyl alcohol and Cyclohexylamine) which, however, gave the poorest yield of the series.

Ammonia can also be made to react in presence of Thoria with the mixed vapours of two alcohols, when, in addition to the simple primary and secondary amines corresponding, a certain proportion of mixed secondary amine also results: for example, Propyl and isoAmyl alcohols with Ammonia, over Thoria at 330° C., give primary and secondary Propylamines, primary and secondary isoAmylamines, and Propyl isoamylamine.

Secondary amines likewise react with alcohols, giving high yields of tertiary amine. Thus, Piperidine in presence of Thoria at 350° C. gives with the appropriate alcohols: *n*-Propyl piperidine, *n*-iso-Amyl piperidine, and, less easily, *n*-Cyclohexyl piperidine, much

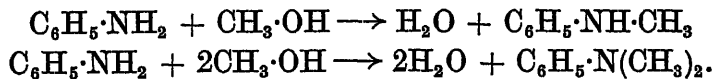
Cyclohexene being produced in this reaction (Gaudion, *Bull. Soc. chim.*, 1911, (4), 9, 417).

The interaction between phenols and Ammonia in contact with dehydrating catalysts is less satisfactory, but low yields of aromatic amines are generally produced. With Phenol and Ammonia, the best catalyst is Alumina at 420° C., when, with excess of the latter and a prolonged period of contact, a yield of Aniline up to 12 per cent. of the theoretical can be obtained. Using Thoria as catalyst, only traces of Aniline are formed, with greater quantities of Diphenyl ether and Diphenylene oxide, as in the absence of Ammonia. When the mixed vapours of Methyl alcohol and Phenol are passed with Ammonia over heated Alumina, a mixture of the Monomethyl and Dimethyl anilines is obtained, the former predominating, but the yields are even smaller than when Phenol and Ammonia alone are used. In presence of Thoria, some Anisole is formed (Briner, Ferrero, and de Luserna, *Helv. Chim. Acta*, 1924, 7, 282).

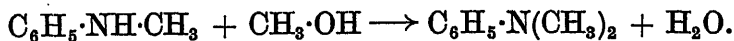
The Cresols react more satisfactorily, and give fair yields of the Toluidines. Thus, when either ortho-, meta-, or para-Cresol is passed with Ammonia over freshly-prepared Alumina at 420° C., the yields of the corresponding ortho-, meta-, or para-Toluidines are 43.1, 40.0 and 42.4 per cent., respectively. These figures rise to 55.1, 51.4, and 52.3 per cent. when the catalyst has been used a short time. Further use, however, diminishes its activity. Resorcinol in the same way gave a 36.9 per cent. yield of meta-Phenylene diamine at first, rising to 53.0 per cent. with use, and then diminishing (Briner, Ferrero, and Paillard, *Helv. Chim. Acta*, 1926, 9, 956).

The Formation of Alkyl Anilines

Mailhe and de Godon found that when a mixture of the vapours of Methyl alcohol and Aniline was passed over Thoria or Zirconia at 400–500° C., condensation to a mixture of Methyl and Dimethyl anilines occurred, while some unchanged Aniline remained,



Using Alumina as catalyst, however, a comparatively small excess of Methyl alcohol only was required to convert the Aniline practically completely into a mixture of the Methyl anilines, and it was also shown that Monomethyl aniline, with Methyl alcohol, easily and completely gave Dimethyl aniline,



The Alumina remained active for a long time, but eventually became brown and somewhat less active. Ignition effected complete regeneration (*C.R.*, 1918, 166, 467).

The Methyl toluidines are made similarly (Mailhe and de Godon, *C.R.*, 1918, 166, 564). When equal parts by weight of Methyl alcohol and ortho-Toluidine are passed over Alumina at 350° C., a mixture of Monomethyl and Dimethyl ortho-toluidines is obtained, and further treatment of this mixture with Methyl alcohol in presence of Alumina at 350° C. converts the whole into pure Dimethyl ortho-toluidine. In the same way, meta- and para-Toluidines give the Mono- and Di-methyl meta- or para-Toluidines. A small proportion of the Methyl alcohol is dehydrated to Dimethyl ether, which is the only bye-product, at temperatures below 400° C.

Mailhe and de Godon have since extended the method to the preparation of methylated Xylidines and Naphthylamines (*C.R.*, 1920, 171, 1154; E.P. 124219 of 1919). All the Xylidines, and α - and β -Naphthylamines, in the form of vapour, with Methyl alcohol, and in contact with Alumina at 360–380° C. give mixtures of the corresponding Mono- and Di-methyl derivatives, the whole of the primary base being methylated. The base was dissolved in the appropriate quantity of alcohol, and vaporised over the catalyst. The relative volumes recommended were as follows: with 2:3-Xylidine, two volumes of Methyl alcohol, or 25 per cent. less in the cases of the 3:4- and 2:5-Xylidines. With α -Naphthylamine, 4 volumes, and with the β -isomer, 10 volumes of alcohol were employed.

This method of methylation of aromatic amines is equally successful for ethylation, using Ethyl alcohol (Mailhe and de Godon, *C.R.*, 1921, 172, 1417). The following amines were dissolved in the necessary proportion of 95 per cent. alcohol: Aniline, the three Toluidines, the Xylidines, α - and β -Naphthylamines and Diphenylamine, and the solution volatilised so that the mixture of vapours in uniform proportions, as mixed, passed over an Alumina catalyst at 350–380° C. Aniline did not ethylate so completely as did Toluidine, and its other Methyl homologues. Very little Ethylene was formed, since the products of reaction almost completely condensed, forming two layers, the lower of which consisted of water, Alcohol, and Ether, while the upper contained the ethylated base, Ether and Alcohol, which were separated by fractionation.

Aniline with two volumes of Alcohol gave a mixture of unchanged Aniline, Monoethyl, and Diethyl anilines, from which the Aniline could be separated as the sparingly soluble sulphate, or by distillation. The higher boiling fraction, consisting principally of Monoethyl and Diethyl anilines, could then be completely ethylated to the latter by three or four successive passages with alcohol over the catalyst. Exhaustive methylation, it may be remarked, requires only one such additional passage.

The three Toluidines were similarly ethylated to Monoethyl and Diethyl toluidines, which one further passage with Alcohol over the

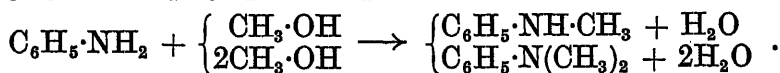
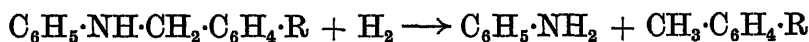
catalyst sufficed to convert completely into the pure diethylated base.

The Xylidines are still more easily ethylated. meta-Xylidine with two volumes of Alcohol readily gave a mixture containing only Mono- and Di-ethyl xylidine : but ortho- and para-Xylidines required two passages with two volumes of Alcohol to react with all the Xylidine. α - and β -Naphthylamines being sparingly soluble in alcohol, a large excess of the latter was needed to form a homogeneous solution convenient for vaporising and admitting to the catalyst. A single passage completely converted the Naphthylamines into a mixture of the mono- and di-ethylated bases. In the same way Diphenylamine, $(C_6H_5)_2NH$, was converted into Diphenyl methylamine, $(C_6H_5)_2N \cdot CH_3$, or Diphenyl ethylamine, $(C_6H_5)_2N \cdot C_2H_5$, by passing with Methyl or ethyl alcohol over Alumina at $360^\circ C$.

A number of new secondary amines of the type



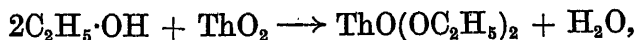
prepared by Mailhe by the hydrogenation of Schiff's bases, were passed with Methyl alcohol vapour over Alumina at $380-400^\circ C$. The tertiary amine sought was in no case obtained, since at the temperature employed the secondary amine decomposed, and in presence of the Methyl alcohol gave methylated derivatives of simpler bases, as follows :



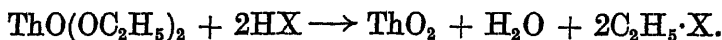
The Hydrogen necessary for the first reaction is obtained by dehydrogenation of Methyl alcohol with simultaneous formation of Formaldehyde (*C.R.*, 1921, 172, 280; *Bull. Soc. chim.*, 1921, IV, 29, 106). Thus, Benzyl aniline, $C_6H_5 \cdot CH_2 \cdot NH \cdot C_6H_5$, passed over the catalyst with excess of Methyl alcohol, yielded a condensate which separated in two layers. The lower was colourless, and consisted of unchanged Methyl alcohol, water, Dimethyl ether, and Formaldehyde. The upper was yellow, and contained Toluene and Dimethyl aniline, with a little Methyl alcohol. In the same way, Benzyl ortho-tolylamine, passed with excess of Methyl alcohol over Alumina at $380-400^\circ C$, gave Toluene, Monomethyl, and Dimethyl ortho-toluidines, while a number of other bases of the same type behaved in an analogous way.

Dehydration between Alcohols and Acids

Assuming that the action of a dehydrating catalyst depends upon a transitory formation of a compound with the hydroxy-body,

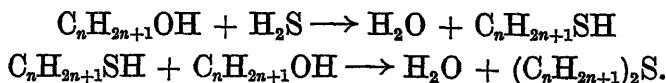


then, if an acidic substance is mixed with the alcohol vapour, a further reaction, as follows, may be expected to occur :

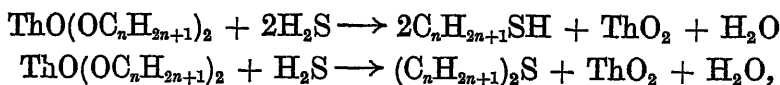


Sabatier and Mailhe realised this expectation for a number of acids, namely Hydrogen sulphide, the halogen acids, and volatile organic acids.

Dehydration between Hydroxy-bodies and Hydrogen Sulphide. When Hydrogen sulphide is mixed with the vapour of a hydroxy-compound and passed over heated Thoria, the two following reactions successively occur :



According to Sabatier and Mailhe, these reactions involve the intermediate formation of a Thoria-Alcohol complex, this then decomposing with Hydrogen sulphide,



more easily than into olefine and water.

The reaction is carried out by passing a mixture of Hydrogen sulphide and the vapour of the hydroxy-body over Thoria, maintained at 300–380° C. The Hydrogen sulphide need not be free from Hydrogen. The product, which can be condensed, consists of a mixture of the mercaptan with varying proportions, generally small, of the sulphide, unchanged hydroxy-body, and water. A certain amount of the hydroxy-body (if alcoholic) suffers dehydration to olefine, but with primary aliphatic alcohols this quantity is not usually great, unless an unnecessarily high temperature has been employed. Secondary alcohols, however, which yield the olefines more easily, generally give a relatively greater proportion of olefine.

By means of this reaction, from the corresponding alcohols Sabatier and Mailhe prepared Methyl, Ethyl, Propyl, 1-Methyl-propyl, 2-Methyl-butyl mercaptans, in yields exceeding 75 per cent. of the theoretical, with smaller amounts of the sulphide. Allyl mercaptan was made in an equally good yield from Allyl alcohol, and Benzyl alcohol gave a good yield of Phenylmethyl mercaptan, with small amounts of sulphide, and Stilbene (*C.R.*, 1910, 150, 1217; Kramer and Reid, *J. Am. C.S.*, 1921, 43, 887).

The yields from secondary alcohols are less, on account of the greater formation of olefine, and rarely exceed 30 per cent. of the theoretical. Sabatier and Mailhe prepared the mercaptans and sulphides from isoPropyl, secondary Amyl and secondary Heptyl

alcohols, Cyclohexanol, the three Methyl cyclohexanols, and Benzhydrol (*C.R.*, 1911, 151, 1217; *Bull. Soc. chim.*, 1912, (4), 11, 99; 1914, (4), 15, 327).

Phenols behave similarly, giving thiophenols, but in still lower yields, the best never exceeding 17 per cent. of the theoretical. Thoria, as before, is the most satisfactory catalyst, and the best working temperature 430—480° C. At higher temperatures, decomposition of the Hydrogen sulphide introduces a complication. Phenol always gives a certain amount of Diphenyl ether.

Other dehydrating catalysts can be used in place of Thoria, but the yields produced are always less. Sabatier and Mailhe compared the action of the various dehydrating oxides in this reaction, using in one case isoAmyl alcohol, and the catalyst at 370–380° C. (*C.R.*, 1910, 150, 1569) and in another, Phenol with the catalyst at 450° C. (*C.R.*, 1910, 150, 1217).

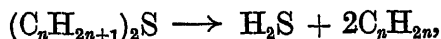
| Catalyst. | Per cent. yields obtainable in dehydration between H ₂ S and | |
|---------------------------------|--|-------------|
| | (a) isoAmyl alcohol. | (b) Phenol. |
| Thoria | 70 | 8 |
| Zirconia | 44 | 1.5 |
| Urania | 30 | 3.8 |
| Blue Tungsten oxide | 22 | 1.5 |
| Chromic oxide | 18 | 2.5 |
| Blue Molybdenum oxide | 17 | 1.8 |
| Alumina | 10 | 0.4 |

In the case of the isoAmyl alcohol, the production of Amylene became greater as the efficiency of the catalyst for mercaptan production diminished.

In the course of this work, Sabatier and Mailhe made the interesting observation that metallic sulphides exert a catalytic action on thio-alcohols similar to that of dehydrating oxides on alcohols. The most effective sulphide catalyst was Cadmium sulphide, which at 320–330° C. afforded a very convenient mode of preparation of the alkyl sulphides,



At a higher temperature, a further molecule of Hydrogen sulphide was eliminated, and an ethylenic hydrocarbon formed,



these reactions presenting a complete analogy with the dehydration of alcohols (*C.R.*, 1910, 150, 1570).

Ethyl mercaptan, passed over Cadmium sulphide at 320° C., gives a high yield of Diethyl sulphide, and at 380° C. is completely decom-

posed into Hydrogen sulphide and Ethylene. isoAmyl mercaptan similarly at 360°C . gives isoAmyl sulphide and at 400°C , Amylene.

With secondary mercaptans, as with secondary alcohols, there is a greater tendency for olefine formation, so that yields of sulphides are smaller. Thus, Cyclohexathiol with Cadmium sulphide at 300°C . gives 12–15 per cent. of Cyclohexyl sulphide, the greater part giving Cyclohexene, which at 360°C . is the exclusive product.

Dehydration between Hydroxy-bodies and Halogen Acids. Sabatier and Mailhe effected the reaction between primary alcohols and Hydrochloric acid gas by passing over Alumina, heated to about 420°C . (*C.R.*, 1919, 169, 122). On account of the difficulty of condensing the product, experiments were not made with Methyl or Ethyl alcohols. It may be stated, however, that these alcohols easily give the pure chlorides, and that the difficulty of condensation may be readily overcome in the case of Ethyl chloride by working under a slight pressure of several inches of Mercury, when pure Ethyl chloride in high yield is obtained. In most cases, from primary aliphatic alcohols, Sabatier and Mailhe obtained the corresponding primary chloride, mixed with some olefine, together with secondary or tertiary chlorides. Thus, when the vapour of normal Propyl alcohol was passed with excess of Hydrochloric acid gas over Alumina at $400\text{--}420^{\circ}\text{C}$., a product which separated into two layers was condensed in an ice-salt bath. The separation was aided by addition of salt, and the upper layer then separated, washed with brine, and with dilute Sodium carbonate solution, dried over granular Calcium chloride and distilled. The chloride obtained was mainly isoPropyl chloride, with a little Propyl chloride. The formation of the secondary chloride was attributed to nearly complete splitting of the normal product into Propylene and Hydrochloric acid, followed by their recombination to isoPropyl chloride. isoButyl alcohol, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{OH}$, similarly gave a good yield of a mixture of 25 per cent. of isoButyl chloride, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\text{Cl}$, and 75 per cent. of Trimethyl chloromethane, $(\text{CH}_3)_3\text{CCl}$; an isomerisation which also occurs when isoButyl chloride is used in a Friedel-Crafts reaction in presence of anhydrous Aluminium chloride. isoAmyl alcohol, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, with Hydrochloric acid gas, in contact with Alumina at 430°C ., gave a little Amylene, and the three chlorides, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$, $(\text{CH}_3)_2\text{CH}\cdot\text{CHCl}\cdot\text{CH}_3$, and $(\text{CH}_3)_2\text{CCl}\cdot\text{CH}_2\cdot\text{CH}_3$, in the proportions approximately of 1 : 2 : 3. Heptyl alcohol, $\text{CH}_3\cdot(\text{CH}_2)_5\cdot\text{CH}_2\cdot\text{OH}$, with excess of Hydrochloric acid, and Alumina at $420\text{--}440^{\circ}\text{C}$. gave a mixture of 1- and 2-Heptenes, the primary and secondary chlorides, and a Diheptene, as well as unchanged alcohol; but at a lower temperature, 380°C ., only 20 per cent. of Heptenes were formed, the main product consisting of the primary chloride.

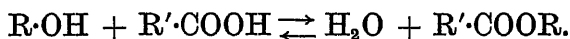
A considerable lowering of the reaction temperature can be obtained

by adding a promoter to the Alumina (1 to 5 per cent. of Zinc chloride) when the isomerisation changes above described are minimised, and the yields of primary chloride considerably increased. Kaolin can be used in place of Alumina.

Sabatier regarded the mechanism of the reaction to consist in the direct interaction of the alcohol and the acid, rather than a preliminary dehydration of the alcohol to the ethylenic hydrocarbon, followed by addition of Hydrochloric acid, basing this view on the fact that secondary alcohols, like isoPropyl, which lose water more easily than the primary alcohols, give comparatively small yields of the corresponding chlorides.

Dehydration between Hydroxyl Bodies and Organic Acids. "Esterification." The usual esterifying agents are concentrated mineral acids, used in proportions of from 1 to 5 per cent. of the reaction mixture undergoing esterification. Such reactions will, however, be more naturally dealt with in considering the use of "condensing agents," and only the application of contact catalysts to esterification considered here.

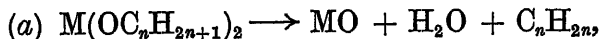
It has long been recognised that the action between a carboxylic acid and an alcohol is reversible,



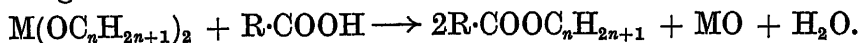
In the absence of a catalyst, these reactions are usually slow. In the presence of a catalyst, however, such as Hydrogen ions in liquid media, or dehydrating oxides in the gas phase, the point of equilibrium may be reached very rapidly. In the latter case, however, when a mixture of the vapours of an alcohol and an organic acid is passed over a heated oxide, such as Thoria or Titania, various changes may occur besides esterification: (1) The acid may undergo the ketone decomposition. Sabatier and Mailhe's theory of dehydrating catalysis would account for this by postulating metallic salt formation between the acid and the catalytic oxide, followed by the well-known pyrogenic decomposition,



(2) The alcohol may give either of two results. According to Sabatier and Mailhe, the action of a dehydrating catalyst on an alcohol consists first in the formation of a metallic complex, $M(OC_nH_{2n+1})_2$. This, in the present instance, may undergo further change as follows:—



(b) React with the acid, regenerating the catalytic oxide and forming an Ester,



These two reactions must both be regarded as reversible and rapid.

When an acid and the catalyst do not interact to any appreciable extent, then only the last reaction can occur, and a good method of esterification results. Thus, a mixture of Benzoic acid with the vapour of either Methyl, Ethyl, Propyl, isoPropyl, isoButyl, isoAmyl or Allyl alcohols, containing at least 12 molecules of alcohol per 1 molecule of acid, when passed over Thoria at 350° C. give 95 per cent. yields of the corresponding benzoates. Secondary alcohols, in spite of the ease with which they give olefines, also give a good yield of benzoate, as shown when isoPropyl alcohol or Cyclohexanol are used. Aliphatic acids cannot be employed with Thoria or Alumina, since the other reactions mentioned occur very extensively, ketones, unsaturated hydrocarbon, or ether being formed, but other aromatic acids, such as the Toluic acids, can naturally be used. Large excess of alcohol brings the equilibrium position to the point of almost complete esterification (Sabatier and Mailhe, *C.R.*, 1911, 152, 358).

Titania at 280–300° C. is an especially satisfactory catalyst for esterification, since it has no action on acids (except formic) with the result that the usual bye-reactions are not induced, and esterification takes place very readily, reaching limits close to those representing the equilibrium proportions, as determined by Berthelot and Menschutkin. It was observed by Berthelot that the equilibrium position in esterification was almost independent of the temperature; a largely increased temperature altering comparatively slightly the composition of the equilibrium mixture—generally in favour of somewhat greater esterification.

The esterification limits obtained between equimolecular mixtures of acid and alcohol, as determined at 155° C. by Menschutkin (*Ann. Chim. Phys.*, 1880, (5), 20, 289; 23, 64), and by Sabatier and Mailhe at 280–300° C. in contact with Titania (*C.R.*, 1911, 152, 358, 494) may be compared.

| Acid. | Alcohol. | Per cent. ester in equilibrium. | |
|------------|----------|---------------------------------|----------------------|
| | | Menschutkin. | Sabatier and Mailhe. |
| Acetic | Methyl | 69.6 | — |
| Acetic | Ethyl | 66.6 | — |
| Acetic | Propyl | 66.9 | — |
| Acetic | Butyl | 67.3 | — |
| Acetic | isoButyl | 67.4 | 69.5 |
| Propionic | Methyl | — | 72.9 |
| Propionic | isoButyl | 68.7 | — |
| Propionic | isoAmyl | — | 72.0 |
| Butyric | Ethyl | — | 71.0 |
| Butyric | isoButyl | 69.5 | — |
| Butyric | isoAmyl | — | 72.7 |
| isoButyric | Ethyl | — | 71.0 |
| isoButyric | isoButyl | 69.5 | — |

The reversibility of the esterification was further noted by Sabatier and Mailhe, who found that by increasing the proportion of one of the reactants more complete esterification resulted. Thus, when 1 molecule of isoButyric acid was passed over the catalyst with 1, 2, and 4 molecules, respectively, of Ethyl alcohol, the corresponding percentages of acid esterified were 71.0, 83.5, and 91.0 per cent. The reverse change was observed when steam and ester were passed over the heated catalyst, the same equilibrium mixture being obtained, or when excess of steam was used, almost complete hydrolysis without appreciable decomposition of acid or alcohol.

Sabatier and Mailhe prepared in this way the Methyl, Ethyl, Propyl, isoPropyl, Butyl, isoButyl and isoAmyl esters of Acetic, Propionic, Butyric, isoButyric, isoValeric, Caproic, Pelargonic and Crotonic acids. Benzyl alcohol also gave satisfactory results with many acids, almost without the simultaneous formation of the resinous dehydration product, $(C_7H_8)_n$. Formates at first could not be obtained, owing to the decomposition which formic acid undergoes at temperatures about 280°C . Later, Sabatier and Mailhe found that esterification often occurred at temperatures much below 280°C ., and that the simpler the interacting molecules of alcohol and aliphatic acid the more rapid was the esterification at any given temperature in contact with a catalyst. From an examination of their results, Sabatier and Mailhe concluded that the rates of esterification were proportional to the velocities of the interacting molecules, as estimated by the kinetic theory. The activity of the catalyst towards all alcohols and fatty acids would therefore be similar, and the rate of esterification depend simply upon the speed of movement of the molecules. This being so, Formic acid should be the easiest of the acids to esterify, and, in fact, it was found that considerable esterification could be effected at temperatures at which it was relatively stable. Considerable quantities of Ethyl formate were obtained by vaporising equimolecular proportions of the alcohol and acid over Titania at 120°C ., while at 150°C ., at which point Formic acid is still stable, equilibrium was almost reached. Methyl, Ethyl, Propyl, Butyl, isoAmyl, and Benzyl formates were prepared in this way.

Secondary and tertiary alcohols, in which the alcoholic function is less marked than in the case of primary, esterify with increasing difficulty when treated by this method. At the same time, dehydration to olefine becomes easier. Thus, in the case of the simplest secondary and tertiary alcohols, isoPropyl, and Trimethyl carbinol, in contact with Titania, the decomposition to olefine commences at 300°C . and 255°C ., respectively. The percentages of these alcohols to be esterified, and the corresponding figures for the isomeric primary alcohols, when passed with an equivalent of the vapour of isoButyric

acid over Titania, are shown in the following table, and illustrate the foregoing general statements :—

| Temp. °C. | Propyl. | isoPropyl. | Trimethyl carbinol. | Primary isoButyl alcohol. |
|-----------|---------|------------|--|------------------------------|
| 235 | 50 | 16.5 | 6 | 22 |
| 256 | — | 21 | } Much decomposition into Butylene. | |
| 292 | 72 | 37 | | |

(Sabatier and Mailhe, *C.R.*, 1911, 152, 1044).

The catalytic activity of Titania for esterification, besides being greater than that of Thoria, is more persistent. Sabatier and Mailhe found that during 20 days, using different alcohols and acids, its vitality had not diminished.

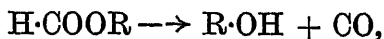
Zirconia as catalyst has been recommended by Mailhe and de Godon (*Bull. Soc. chim.*, 1921, 29, 101; *Caoutchouc et Guttapercha*, 1921, 18, 80679), who claim that it is superior to Titania. The optimum temperature is stated to be about 280–290° C., when esterification can be easily carried to the equilibrium point, resulting in nearly complete reaction if a fair excess of one of the reacting substances is employed. In this way, the following esters were made: Ethyl acetate, Propyl acetate, isoButyl acetate, isoAmyl acetate, Ethyl propionate, Propyl propionate, Propyl butyrate, Propyl valerate, Propyl caproate, isoPropyl propionate, and isoPropyl butyrate. Increasing the proportion of alcohol above the equimolecular much increased the conversion. Thus, in a tube 120 cm. long, containing 244 grams of Zirconia at 280–290° C., an equimolecular mixture of the vapours of Ethyl alcohol and Acetic acid at the rate of 40 c.c. per minute gave 71 per cent. conversion into the ester. Four times this proportion of Ethyl alcohol, under the same conditions, esterified 99 per cent. of the acid.

Zirconia maintains its activity for a long time, without any apparent surface change. The interior may become grey, but ignition restores its white colour and full activity.

According to Milligan and Reid, Silica gel is a still better catalyst than either Titania or Zirconia ("Catalysis," Reid, 1923). Beryllium oxide has been employed by Hauser and Klotz, and high yields of esters from primary, secondary, and tertiary alcohols have been obtained, including some of considerable structural complexity (*Chem. Zeit.*, 1913, 37, 146).

Esters of higher acids can also be made by passing an ester of Formic acid, mixed with the other acid, over a suitable catalyst. Titania at 250° C. is the best catalyst, but Thoria at a rather higher temperature, 300–330° C., can also be used. Under these circum-

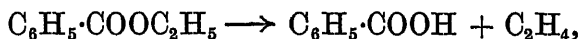
stances, the formate decomposes into the corresponding alcohol and Carbon monoxide,



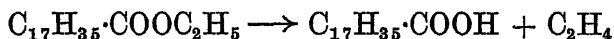
the former then esterifying the other, and more stable, acid. In this way from Methyl formate and isoButyric acid, using Titania at 250° C., isoButyric methyl ester and Carbon monoxide are obtained, together with a little Methyl alcohol and isoButaldehyde, the last-named arising from reduction of the acid with Formic acid, while from Methyl formate and isoValeric acid, using Thoria at 300–330° C., Methyl isovalerate and isoValeraldehyde are obtained. In the latter case, on raising the temperature, isoValerone soon commences to be formed by the ketonic decomposition of the acid (Sabatier and Mailhe, *C.R.*, 1912, 154, 175).

Action of Dehydrating Catalysts upon Esters. If in the esterification reactions just described the temperature of the catalyst is raised, the esters first formed are decomposed. The decomposition may proceed along several alternative routes, the particular one predominating depending upon the ester.

In the absence of a catalyst, esters are fairly stable up to high temperatures. Colson found that in a sealed tube at 300° C., Ethyl benzoate slowly decomposed to Benzoic acid and Ethylene,

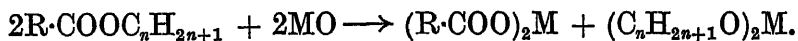


and Ethyl stearate to Stearic acid and Ethylene,



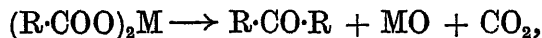
(*C.R.*, 1908, 147, 1054), and regarded this reaction as a general one.

In the presence of catalysts, the decomposition of esters is much facilitated. The above reaction is not, however, the only one that may occur, different catalysts and different esters giving different results. The course of the decomposition reactions that esters may undergo can be most conveniently studied if we suppose, in accordance with the theory of Sabatier and Mailhe, that compounds are first formed by combination both of the alcohol and the acid with the catalyst,



The metallic compounds so formed are unstable at the temperature employed (especially if the metallic oxide used as catalyst catalyses the decomposition of either acid or alcohol), and the following further changes then take place (Sabatier and Mailhe, *C.R.*, 1911, 152, 669; 1912, 154, 49, 175).

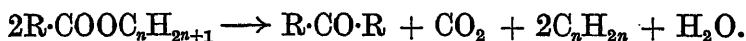
(1) If both metallic compounds are decomposed with about equal ease, then from the acid compound, ketone and Carbon dioxide are formed,



and from the alcohol compound, olefine and water,

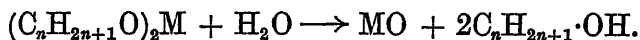


the volume of the olefine obtained being approximately double the volume of Carbon dioxide,



This is usually the predominant course of reaction when Alumina at 380–400° C. is used as catalyst. If the ester is a methyl ester, then Dimethyl ether, instead of an olefine and water, is formed (Senderens, *Bull. Soc. chim.*, 1909 (4), 5, 482).

(2) When the catalyst decomposes acids more actively than alcohols, the ketone formation is faster than olefine formation. Moreover, water formed in the alcohol decomposition has time to hydrolyse an equivalent amount of alcohol-metallic complex, giving the alcohol,



The combined effect of acid and alcohol decomposition then becomes

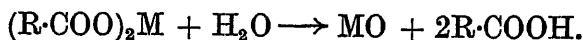


that is, equivalent quantities of alcohol and ketone, and equal volumes of Carbon dioxide and olefine are produced. This type of decomposition occurs when Thoria at 310° C. is used as catalyst with the following esters: Ethyl acetate, Propyl acetate, Propyl propionate, isoButyl acetate, Ethyl caproate.

As the temperature is raised, the decomposition of the intermediate metallic compounds increases, with the result that type (2) decompositions tend to approach more closely to type (1), hydrolysis to alcohol having less time to occur, as, for example, when isoButyl acetate is passed over Thoria at 350° C., or Ethyl caproate over Thoria at 360° C. At the same time, when high temperatures are used, the alcohol tends to be dehydrogenated, so that aldehydes and Hydrogen appear among the products together with the decomposition products, saturated hydrocarbon and Carbon monoxide, of the former.

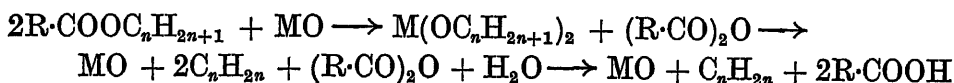
(3) When the catalyst is more active towards the alcohol, decomposition of the complex $(C_nH_{2n+1}O)_2M$ proceeds faster than that of the complex $(R \cdot COO)_2M$, which produces ketones relatively slowly.

Water formed by the alcohol decomposition then has time to hydrolyse the acid metal complex,



Here, then, the formation of ketone is diminished, the acid replacing it to a larger or smaller degree, while unsaturated hydrocarbon is formed in quantity equivalent to the ester used. Action follows this course when Titania at 400°C . is used as catalyst with esters of aliphatic acids (which, as we have found, are fairly stable with Titania) such as Acetic, Propionic, Butyric, isoButyric, and Valeric acids, which give Carbon dioxide and olefine, ketone and acid.

(4) A limiting case of the preceding is where the catalyst cannot decompose the acid, but is able to decompose the alcohol. Here the acid is completely regenerated, while the alcohol undergoes more or less complete dehydration to the olefine and water. This was the action observed by Colson, already referred to. It happens with esters of aromatic acids, *e.g.*, Benzoic or the three Toluic, when Thoria or Titania above 400°C ., or many other substances are used as catalysts; also in the case of aliphatic esters when Boric anhydride above 400°C . is the catalyst, since this substance is catalytically inert towards all acids. The course of the reaction may be expressed thus:



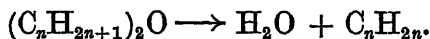
(Sabatier and Mailhe, *C.R.*, 1911, 152, 669; Mailhe, *Chem. Zeit.*, 1911, 35, 485, 507).

Methyl esters are generally more difficult to decompose than other esters, and cannot yield an olefine. Dimethyl ether is often formed instead, the products being Carbon dioxide, a ketone, and Dimethyl ether; but at the higher temperature which Methyl esters require, some decomposition occurs, the water formed saponifying a certain proportion of the ester to Methyl alcohol and acid.

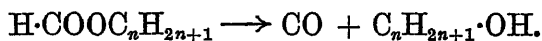
5. *The Formic Esters.* These generally decompose in a manner quite different from esters of the higher acids. In the absence of catalysts, Formic esters are stable up to 400°C ., or higher, but in contact with catalysts which assist the decomposition of Formic acid, decomposition occurs at temperatures below those necessary in the case of other esters, though higher than are required in the case of Formic acid itself. Sabatier and Mailhe have shown that below 400°C . this decomposition takes place along two directions simultaneously (*C.R.*, 1912, 154, 49). (a) The ester undergoes a reaction analogous with the ketone decomposition of other esters,



Under conditions where the ether is stable, *i.e.*, when Methyl formate is used, the ether is obtained as such. In all other cases, it is partially or completely dehydrated to olefine and water,



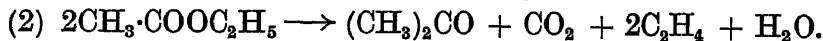
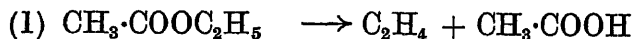
(b) The reaction which always predominates in the decomposition of Formic esters is the following :



A portion of the alcohol at the same time is decomposed, either to aldehyde and Hydrogen, or to olefine and water, or to all four simultaneously, according to whether the catalyst is dehydrogenating or dehydrating, or both. Water formed also hydrolyses some of the ester, liberating Formic acid, so that this or its decomposition products are also obtained.

Reaction (a) is most pronounced with a Thoria catalyst, but even so, (b) is predominant, and becomes more and more so as the temperature is raised. Zinc oxide effects mainly (b), but water formed hydrolyses a considerable proportion of ester to acid, which the Zinc oxide then decomposes to Carbon dioxide. Titania gives (b) almost exclusively, that is, from Methyl formate are formed Carbon monoxide, Methyl alcohol, Dimethyl ether (by dehydration), and Formic acid (by hydrolysis), and since Formic acid in contact with Titania gives only Carbon monoxide and water, the gas obtained in the decomposition of Formic esters with Titania is almost pure Carbon monoxide. Finely-divided metals are most active with Formic esters, Nickel reacting at 220° C., Platinum at 270° C., and Copper at 350° C. Reaction (b) is again the chief, but the alcohol is quickly dehydrogenated to aldehyde, which, in the cases of the Nickel or Platinum catalysts (unless the temperature is very low) is completely decomposed to hydrocarbon and Carbon monoxide, isolation of the aldehyde only being possible when Copper is used.

Adkins has shown that the mode of preparation of catalysts much influences the relative rates at which the different decompositions of an ester may be induced. Thus Titania, as we have seen, catalyses the following decompositions of Ethyl acetate :

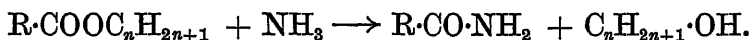


If the Titania is made by precipitation of the hydroxide from the sulphate, the decomposition proceeds two-thirds along the first course and one-third along the second. When the Titania is made by precipitating blue Titanous hydroxide from Titanous chloride, and allowing this in suspension to oxidise to the white Titanic hydroxide,

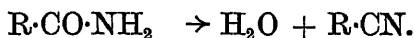
then the reaction proceeds one-third along the first course and two-thirds along the second. Alumina also, according to its mode of preparation and the time it has been used, induces, to different degrees, decomposition of esters according to types (1) and (2). Thoria, when prepared by ignition of the nitrate, is of little use for preparation of Ethylene (Sabatier), but made from precipitated hydroxide gives with Ethyl acetate almost theoretically the reaction



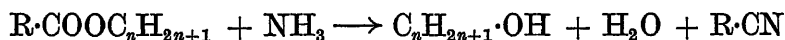
Reaction between Esters and Bases in Contact with Dehydrating Catalysts. When a carboxylic ester is treated with Ammonia, interaction leads to formation of the acid amide, and liberation of the alcohol of the ester,



The resulting amides, on dehydration, for example with Phosphoric anhydride, yield the corresponding nitrile



Mailhe has shown that in presence of a dehydrating catalyst these reactions occur easily, the former at a comparatively low temperature, while at higher temperatures the latter is effected simultaneously, with formation of a good yield of nitrile. Thus, when an ester vapour, mixed with Ammonia, is passed over Alumina, Zirconia, or, best of all, Thoria, at a high temperature, elimination of water and alcohol results in almost complete conversion into a good yield of nitrile,



(*C.R.*, 1918, 166, 36; *Bull. Soc. chim.*, 1918, IV, 23, 235; *Caoutchouc et Guttapercha*, 1919, 16, 9947).

The method is general for both aliphatic and aromatic esters. A mixture of the vapour with Ammonia, in equimolecular proportions, or containing excess of the latter, is passed over a suitable catalyst, generally Alumina or Thoria, at 450–490° C., and the product condensed. The condensate usually separates into two layers, the lower aqueous and the upper containing the nitrile. Aldehydes, aldehyde-ammonias, Hydrogen, and olefines which are formed are derived from the alcoholic group, while some amide usually escapes complete dehydration to nitrile, and appears in the product. Using an Alumina catalyst, Ethyl esters usually give Hydrogen and Ethylene in approximately the ratio of 1 : 2.

The following esters were converted into nitriles, using Thoria or Alumina at 450–490° C., the rather higher temperature being

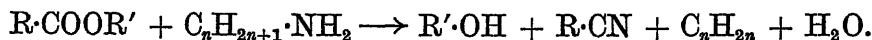
required for the latter catalyst. The Ethyl and Amyl esters of iso-Valeric acid, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{COOH}$, gave the corresponding Valero nitrile, $(\text{CH}_3)_2\text{CH}\cdot\text{CH}_2\cdot\text{CN}$. Ethyl, Propyl, and isoButyl butyrate gave Butyronitrile, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN}$, and isoButyl and isoAmyl propionates gave Propionitrile, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CN}$, while Phenyl acetic Methyl and Ethyl esters gave Phenyl acetonitrile, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CN}$ (*C.R.*, 1918, 166, 121; *Bull. Soc. chim.*, 1918, 23, 232).

Aromatic esters behaved similarly, dehydrating to nitriles in exceptionally high yields in contact with Alumina or Thoria at 450–480° C., thus: Methyl, Ethyl, Propyl, isoPropyl, and isoAmyl benzoates with Ammonia gave Benzonitrile; ortho-, meta-, and para-Toluic methyl esters, $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{COOCH}_3$, gave ortho-, meta-, and para-Toluic nitriles, respectively, and α - and β -Naphthoic methyl esters the corresponding α - and β -Naphthonitriles. The method is equally satisfactory with unsaturated esters, these dehydrating to the corresponding unsaturated nitriles when passed with Ammonia over Alumina at 490–500° C., thus, Crotonic ester, $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{COOC}_2\text{H}_5$, gives Crotononitrile, $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CN}$; Ethyl cinnamate,



gives Cinnamonitrile, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CN}$, Methyl oleate gives Oleonitrile, $\text{C}_{17}\text{H}_{33}\cdot\text{CN}$, and Elaidic ester gives Elaidonitrile, $\text{C}_{17}\text{H}_{33}\cdot\text{CN}$. In each case the product separated into two layers, the lower aqueous, while the upper, on drying over Calcium chloride and distilling, yielded alcohol, aldehyde, nitrile, and untransformed ester. The gas evolved (in the case of the ethyl esters) consisted mainly of Ethylene, with a little Hydrogen (Mailhe, *Bull. Soc. chim.*, 1920, 27, 226).

Amines can replace Ammonia in this reaction. Thus, when the vapour of an ester is passed with an equimolecular proportion of a primary amine over Alumina at 500° C., a mixture of nitrile, alcohol, and unsaturated hydrocarbon results:

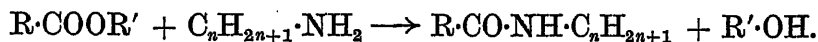


At lower temperatures, some of the substituted acid amide may escape dehydration, and appear among the products.

With Ethylamine, $\text{C}_2\text{H}_5\cdot\text{NH}_2$, Methyl benzoate gave Benzonitrile; isoAmyl valerate gave Valeronitrile, and para-Methyl benzoic methyl ester, para- $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{COOCH}_3$, gave para-Methyl benzonitrile, para- $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{CN}$. In this case, at 440–450° C., much amide, para- $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_2\text{H}_5$, appeared with the nitrile. In the same way, isoAmylamine reacted with Methyl benzoate in presence of Alumina at 470–480° C., giving Benzonitrile, but in poor yield, and with isoButyric methyl ester to give isoButyric nitrile. Likewise Ethyl benzoate with $(\text{C}_3\text{H}_7)_2\text{CH}\cdot\text{NH}_2$, and Alumina at 480° C. gave Benzonitrile (*C.R.*, 1920, 170, 813).

The isolation of the amide stage in this reaction is not always easy, but at lower temperatures than are necessary for the dehydration to nitrile, good yields of amide (or substituted amide) can often be obtained. This reaction readily takes place in liquid media at a moderate temperature, when Ammonia, or aliphatic amines are heated with esters, but weak bases, such as aromatic amines, react only slowly, or not at all in the "wet" way; even though, with the free acid, the weakest bases will generally produce an amide on boiling, or raising to a sufficient temperature for the reaction.

By the catalytic method, Mailhe was able easily to effect the interaction between aromatic amines and esters to amides, passing equimolecular proportions over Alumina or Thoria at 450–490° C.,

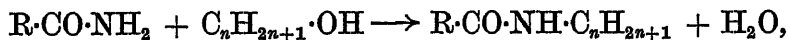


In this way, Mailhe obtained Benzanilide (from Aniline and Methyl or Ethyl benzoate), the three Benzotoluidides (from Benzoic esters and the corresponding Toluidine), Benzocyclohexylamide (from Methyl benzoate and Cyclohexylamine), Phenyl-propionanilide (from Phenyl propionic ester and Aniline), Cuminanilide (from Cuminic ester and aniline), and the anilides of a number of fatty acids. Salicylic methyl ester and Ammonia, even at 500° C., did not commence to form nitrile, Salicylamide only being formed. In most cases, nitrile was produced simultaneously with the amide, the amount increasing with rise of temperature.

In place of the esters of acids, the anhydride of the acid can be used, when, in contact with Alumina or Thoria at 450° C., the amides, not the nitriles, are formed. As before, at a higher temperature the main product is the nitrile. Thus, from the anhydrides of Propionic and isoValeric acids, with Ammonia, and the catalyst at 450° C., Propionamide and isoValeramide were obtained.

Similarly, the esters can be replaced by the acid chlorides. The acid chlorides and Ammonia readily give acid amides, which, in contact with a dehydrating catalyst at a sufficiently high temperature, are further changed to nitriles. Thus, from Benzoyl, isoValeryl, isoButyryl, and Propionyl chlorides, Mailhe obtained excellent yields of the corresponding nitriles (*Bull. Soc. chim.*, 1918, (IV), 23, 380).

Substituted amides cannot be made by dehydration between an acid amide and an alcohol in accordance with the equation,



because the water formed hydrolyses the amide, and reaction then takes an entirely different course (Mailhe, *Bull. Soc. chim.*, 1923, IV, 33, 81).

✓ *Dehydration between Carbon Monoxide and Ammonia.* When a mixture of Carbon monoxide and Ammonia is passed over Alumina at 450–550° C., Zirconia at a somewhat lower temperature, or Thoria at 400° C., the Carbon monoxide functions in a way suggestive of "Formic anhydride," giving Hydrocyanic acid (Formic nitrile), which combines with excess of Ammonia to produce Ammonium cyanide,



With Thoria as catalyst the yield is nearly quantitative, while without a catalyst the reaction is hardly appreciable even at 600° C., and at a red heat, though faster, much carbonisation occurs (Mailhe and de Godon, *Bull. Soc. chim.*, 1920, IV, 27, 737).

Dehydration between Carbonyl Compounds and Ammonia. When an aldehyde-ammonia or an aldehyde vapour mixed with Ammonia is passed over Thoria at 420–440° C. the corresponding nitrile and water are formed, together with unidentified, high-boiling, alkaline condensation products of the aldehyde and Ammonia. With the exception of Formaldehyde and Acetaldehyde, the method is of general application for both aliphatic and aromatic aldehydes, but on account of bye-reactions the yields are not high,

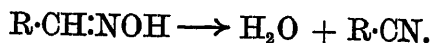


(Mailhe and de Godon, *C.R.*, 1918, 166, 215). In this way, the following aldehydes were converted: Propionic aldehyde, $\text{C}_2\text{H}_5\cdot\text{CHO}$, into Propionitrile, $\text{C}_2\text{H}_5\cdot\text{CN}$; isoButyric aldehyde, $(\text{CH}_3)_2\text{CH}\cdot\text{CHO}$, into isoButyronitrile, $(\text{CH}_3)_2\text{CH}\cdot\text{CN}$; isoValeric aldehyde, $(\text{CH}_3)(\text{C}_2\text{H}_5)\text{CH}\cdot\text{CHO}$, into isoValeric nitrile, $(\text{CH}_3)(\text{C}_2\text{H}_5)\text{CH}\cdot\text{CN}$; Benzaldehyde, $\text{C}_6\text{H}_5\cdot\text{CHO}$, into Benzonitrile, $\text{C}_6\text{H}_5\cdot\text{CN}$; and para-Methoxybenzaldehyde, $\text{CHO}\cdot\text{C}_6\text{H}_4\cdot\text{OCH}_3$, into para-Methoxy benzonitrile, $\text{CH}_3\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CN}$.

According to the above equation, the first effect of dehydration between an aldehyde and Ammonia is the formation of an imine, which, however, cannot in general be isolated. According to Mignonac, when a ketone is vaporised with Ammonia over Thoria at 300–400° C., imines again are first formed. The purely aliphatic ketones, however, gave ketimines which could not survive the conditions of reaction, undergoing further condensation, so that none could be isolated. With aromatic ketones, however, ketimines were prepared in this way, namely, $(\text{C}_6\text{H}_5)(\text{CH}_3)\text{C}\cdot\text{NH}$ from Acetophenone; $(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)\text{C}\cdot\text{NH}$ from Propiophenone, and $(\text{C}_6\text{H}_5)_2\text{C}\cdot\text{NH}$ from Benzophenone. Cyclohexanone gave a very small yield of Cyclohexylimine, $\text{C}_6\text{H}_{10}\cdot\text{NH}$ (Mignonac, *C.R.*, 1919, 169, 237).

Dehydration of Oximes. Oximes are easily dehydrated by contact

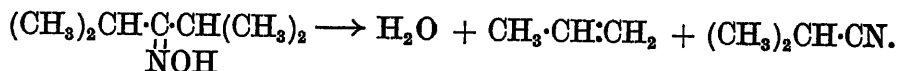
of their vapours with Alumina or Thoria at 340–360° C., the corresponding nitrile being formed,



The decomposition is more complex than the equation indicates, however, since Hydrogen, olefines, Ammonia, amines, and high-boiling basic condensation products are also formed (Mailhe and de Godon, *Bull. Soc. chim.*, 1918, IV, 23, 18).

(a) *Aldoximes*. When isoValeraldoxime, $(CH_3)_2CH\cdot CH_2\cdot CH\cdot NOH$, was vaporised over precipitated Alumina at 350–370° C. a liquid product was condensed which separated into two layers. The lower layer was aqueous, while the upper consisted mainly of isoAmyl nitrile, $(CH_3)_2CH\cdot CH_2\cdot CN$, which was identified by reduction to the isoAmylamines by passage with Hydrogen over catalytic Nickel at 200° C. Oenanthaldoxime, $CH_3(CH_2)_5\cdot CH\cdot NOH$, in the same way with Alumina at 350–360° gave Heptonitrile, $CH_3(CH_2)_5\cdot CN$, identified by hydrogenation to the Heptylamines with Hydrogen and Nickel at 200° C. Thoria effected the same reactions at a somewhat lower temperature, 340–350° C.

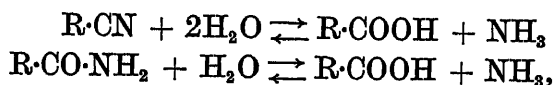
(b) *Ketoximes*. The dehydration of ketoximes, not easily accomplished by chemical agents, gives fair yields of nitriles (less rich in Carbon than the original oxime) by the catalytic method in the following two cases, at least. IsoButyrone oxime, $[(CH_3)_2CH]_2C\cdot NOH$, vaporised over Thoria or Alumina at 350–360° C., gives a gaseous and a liquid product. The former is mainly Propylene, while the latter separates into two layers, the lower aqueous, the upper consisting mainly of isoButyronitrile, $(CH_3)_2CH\cdot CN$,



IsoValerone oxime, $[(CH_3)_2CH\cdot CH_2]_2C\cdot NOH$, in the same way with Thoria or Alumina at 360–380° C., gives isoValeric nitrile, $(CH_3)_2CH\cdot CH_2\cdot CN$.

The many methods available for the preparation of nitriles, largely due to the investigations of Mailhe and his collaborators, have been reviewed in detail by Mailhe (*Ann. Chim.*, 1920, 13, 183–228).

Hydrolysis of Amides and Nitriles. The well-known reverse changes of the ones we have been detailing, namely, the hydrolysis of nitriles or of amides to the corresponding acids and Ammonia,

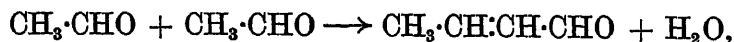


which are usually effected catalytically by the action of acids or alkalis (Hydrogen or Hydroxyl ions), can also be brought about by

contact with dehydrating catalysts. Thus, when steam and the vapour of a nitrile are passed over Alumina or Thoria at about 420°C ., hydration occurs, with formation of the corresponding acid, which, however, may undergo (in the case of fatty acids) the usual ketone decomposition. Thus, from Benzonitrile, ortho-, meta-, and para-Tolunitriles, $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{CN}$, the corresponding acids, Benzoic, or ortho-, meta- or para-Toluic, were obtained. β -Naphthyl cyanide, $\text{C}_{10}\text{H}_7\cdot\text{CN}$, similarly gave β -Naphthoic acid, $\text{C}_{10}\text{H}_7\cdot\text{COOH}$; Benzyl cyanide, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CN}$, and Phenyl propionitrile, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CN}$, gave, respectively, Phenyl acetic and Phenyl propionic acids, and Valeric nitrile, $\text{C}_5\text{H}_{11}\cdot\text{CN}$, gave Valeric acid (Mailhe, *C.R.*, 1920, 171, 245; *Bull. Soc. chim.*, 1920, 27, 754).

Dehydration between Aldehydes and Ketones. "Crotonisation." Carbonyl compounds tend with greater or less ease to undergo condensation, two or more molecules combining with elimination of water. This is usually brought about by use of "condensing agents" in liquid media, changes which may be discussed in the appropriate place. Contact agents can also bring about the same reaction, which is described as "crotonisation" from the simplest aldehyde, Crotonic, which can be prepared by this method.

Acetaldehyde, $\text{CH}_3\cdot\text{CHO}$, or, better, Paraldehyde, when passed over Thoria, Titania, or preferably Uranium oxide at 300°C . or higher, is partly condensed as follows:



while a considerable proportion yields higher condensation products, which also are less stable unsaturated aldehydes (Sabatier and Gaudion, *C.R.*, 1918, 166, 632). This reaction can conveniently be carried out by passing alcohol vapour first over a layer of Copper at 250°C ., to produce the Acetaldehyde, then over one of the "crotonising" catalysts, or alternatively, a slow current of Alcohol can be used, and Uranium oxide at $360\text{--}400^{\circ}\text{C}$., when the two reactions occur together. The mixture of products obtained in the reaction, when reduced in contact with active Nickel, yields mainly Butyl alcohol and Hexanol, these being derived from Crotonaldehyde and the diethylenic aldehyde, $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CHO}$, respectively, but evidence of still more extensive condensation was afforded by the presence of smaller quantities of Octanol, Decanol, and a phenolic compound.

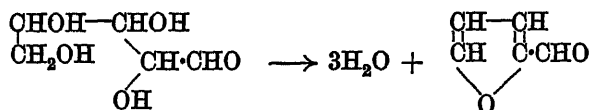
Sabatier and Gaudion obtained similar results to the foregoing when Glycerine was passed over Alumina at 360°C ., the first dehydration product being Acrolein, which then formed more complicated aldehydic condensation products. Finely-divided Copper at 330°C . also dehydrated Glycerine, the product, however, being mainly Acrolein, Ethyl alcohol, and Allyl alcohol, with small amounts of

Methane and Carbon monoxide. In each case, the product of dehydration, on hydrogenation with Nickel, yielded a mixture of aliphatic alcohols boiling between 80° and 235° C., from which Ethyl and Propyl alcohols were isolated (*C.R.*, 1918, 166, 1033).

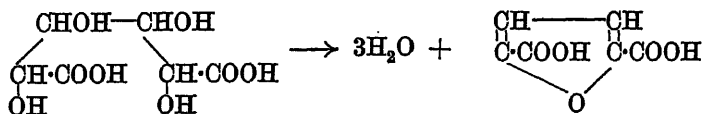
Condensations accompanied by elimination of water, such as that between carbonyl compounds, are very common in organic chemistry, and are usually carried out in liquid media, a substance in solution serving as catalyst, or "condensing agent," *e.g.*, to mention a few, the formation of Formaldehyde and phenol condensation products ("Bakelite," etc.); condensation of aldehydes with alcohols to acetals; the internal condensation of ortho-Benzoyl benzoic acid and its derivatives to Anthraquinone and its homologues, and the reaction between Formaldehyde and many Benzene or Naphthalene derivatives to give "methane bases" derived from Diphenylmethane. The use of contact catalysts in such reactions as these may be possible, but the subject does not appear to have been investigated; probably because the heterogeneous method would have no advantage over the homogeneous.

Ring formation by Dehydration

Cyclic structures containing five or six members are fairly easily formed by elimination of water between two hydroxyl groups. Thus γ -hydroxy-acids easily form lactones, and the action is catalysed by the presence of acids. Arabinose on prolonged boiling with 30-35 per cent. Sulphuric acid gives Furfuraldehyde by loss of three molecules of water:



(Stone and Tollens, *Ann.*, 1888, 249, 237). Mucic acid or Saccharic acid heated to 100° C. in a closed vessel with Hydrochloric acid loses three molecules of water and gives Furfurane $\alpha\alpha'$ -dicarboxylic ("Dehydromucic") acid,

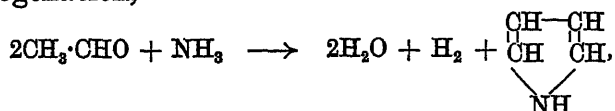


(Yoder and Tollens, *Ber.*, 1901, 34, 3446).

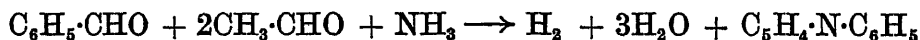
When Ammonia or Sulphuretted hydrogen is passed with hydroxy-bodies over dehydrating catalysts, heterocyclic structures containing Nitrogen or Sulphur in the ring are very commonly formed, though generally in only small amounts. Thus, in the ordinary amine

synthesis from an alcohol and Ammonia, homologues of Pyridine or of Pyrrole are formed. Such syntheses are probably very common, since by virtue of their great stability cyclic structures tend to result from pyrogenic reactions, and in presence of Ammonia or Sulphuretted hydrogen atoms of Nitrogen or Sulphur generally enter into the ring structure. This accounts for the formation of heterocyclic Nitrogen or Sulphur containing rings during distillation of coal; and the large proportion of homologues of Pyridine found in bone oil. Presence of catalysts may considerably influence these syntheses.

Acetaldehyde and Ammonia when passed over Alumina below 300° C. give a certain amount of Pyrrole by simultaneous dehydration and dehydrogenation,



while a mixture of the vapours of Benzaldehyde and Acetaldehyde passed with Ammonia over Alumina at a higher temperature gives α - and γ -Phenyl pyridines,



(Tschitschibabin, *J. Russ. Phys. Chem. Soc.*, 1915, 47, 703).

CHAPTER XII

THE UTILISATION OF COAL

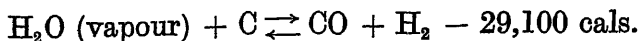
Introduction. Water Gas and its Reactions. Replacement of Carbon Monoxide with Hydrogen: (a) The Badische Continuous Catalytic Process; (b) The Griesheim-Elektron Process. The Catalytic Reduction of Carbon Monoxide. The Catalytic Reduction of Carbon Dioxide. Technical Applications of the Catalytic Reduction of Oxides of Carbon. Production of Methane. Syntheses from Carbon Monoxide and Hydrogen. Historical. The Production of Petroleum: (a) Synthol; (b) Synthesis; (c) Fischer and Tropsch's Ordinary Pressure Synthesis. The Manufacture of Methyl Alcohol. The Bergius Process.

MANY factors are contributing at the present time towards the realisation of a complete change in the methods of utilising raw coal: (1) The increasing quantities of liquid fuels required, and the consequent necessity for those countries not possessing natural supplies, of producing an artificial substitute. (2) The importance of many of the products of coal distillation in chemical and other industries. (3) Coal now is not a cheap fuel nor, compared with liquids or gases, a convenient one, either from the point of view of manipulation or transport. (4) Atmospheric pollution, with its serious consequences on climate, vegetation, urban amenities, and human health, is largely the result of burning crude coal.

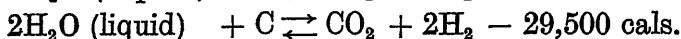
It may be surmised that the increased yield of gaseous and liquid products, together with the easily combustible and smokeless coke, obtained by low temperature carbonisation of coal, will eventually result in one of the newer processes (at present in an advanced experimental stage) superseding the older existing gasworks practice. At the same time, even with the increased yield of volatile fuels obtained by low-temperature carbonisation, the requirements of these substances cannot be fully met, and a balancing process whereby they can be obtained in quantities as desired from other coal products is called for. In several directions, all employing catalytic agents, results of great significance are accumulating, as follows: (1) Franz Fischer's processes, commencing with water gas, the product of reaction between steam and coke. (2) The Bergius process, from coal, by hydrogenation at high pressure. (3) New processes for the manufacture of pure organic substances—for example, Methyl alcohol—by contact of purified water gas at high pressure with a suitable catalyst.

Reactions with Water Gas

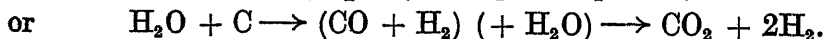
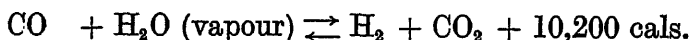
When steam is passed over heated Carbon, interaction occurs, with formation of Hydrogen and Carbon monoxide,



This reaction occurs at a high temperature. When the Carbon is activated by addition of a catalytic agent, or if it is spread in a finely-divided form, action can be made to occur at a lower temperature, when it takes the following further course to an extent increasing as the temperature is lowered,



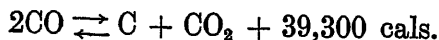
In practice, when it is desired to effect the second stage of the reaction, it is usually preferable to bring this about independently by passing Carbon monoxide or water gas with excess of steam over a suitable catalyst, usually Iron oxide with a promoter, when conditions of temperature and concentration can be more advantageously adjusted than is possible when the two reactions are attempted together,



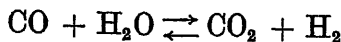
These are the fundamental reactions underlying the manufacture of water gas. Other fundamental reactions are the producer gas reaction, between Carbon dioxide and Carbon at a high temperature, whereby Carbon monoxide is formed,



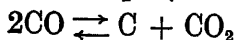
and the reverse of this, which occurs when Carbon monoxide is passed alone over metal catalysts, especially Nickel,



From the thermal values it will be seen that the equilibria in the reactions



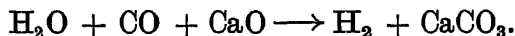
and



are displaced towards the right by lowering the temperature. In the case of the first, this displacement is very considerable, as values for the equilibrium constant, given later, show. The second equilibrium was shown by Fester and Brude to be displaced but little when, by use of an active catalyst, it was attained at a lower temperature (*Ber.*, 1923, 56B, 2245).

From the foregoing, it will be apparent that water gas prepared at a high temperature will consist of Carbon monoxide and Hydrogen in approximately equivalent proportions, while at lower temperatures a larger percentage of Hydrogen will be present and an increasing proportion of Carbon dioxide appear, consequent upon the second stage of the reaction commencing. Below 800°C . ("low temperature water gas"), the Carbon monoxide almost vanishes, the product approximating to a mixture of Carbon dioxide and Hydrogen in the volume proportions of 1 to 2. At such temperatures, however, reaction between steam and Carbon is impracticably slow, unless means are adopted to augment it. The method of D.R.-P. 259030 proposes to achieve this by reacting upon Carbon with liquid water under high pressure, at about 360°C . in presence of a catalyst soluble in water, such as Thallium chloride. The gases produced are almost exclusively Hydrogen and Carbon dioxide in the proportions by volume of 2 to 1. The latter can be removed by water scrubbing or other means (the gases being already at high pressure), when the former is obtained in a state of fair purity. A considerable rate of production by this method is claimed.

The presence of alkalis in the Carbon lowers the temperature at which it is attacked by steam to a point ($500\text{--}600^{\circ}\text{C}$.) at which Carbon dioxide and Hydrogen are the chief products. This forms the basis of the method of Hydrogen manufacture named after the Chemische Fabrik Griesheim-Elektron, who patented the use of lime and other alkalies for effecting the second stage of the water gas reaction,



This process will be dealt with later. It is clear that if the alkali is impregnated within the Carbon, then the two stages of the water-gas reaction can be conducted together.

In technical practice, the most economical means of production of water gas consists in passing alternate blasts of air and steam through a bed of hot Carbon, usually in the form of coke. During the air-blast period the Carbon is raised by the heat of combustion to a high temperature, a fuel gas of low calorific value (air-producer gas) being formed by the blast. In the steaming periods, the heat stored in the mass, now at a high temperature, is employed in effecting the water gas reaction, the gaseous products of the steaming periods being collected separately. Almost all the numerous types of water gas plants employ this procedure, so that the resulting water gas, formed over a range of temperatures, varies in composition during the steaming according to the prevailing temperature of the Carbon, but since the rate of production is much greater at high temperatures, the average composition of the product approaches closely to that of high temperature water gas, being

mostly Carbon monoxide and Hydrogen containing a slight excess of the latter and a small proportion only of Carbon dioxide. Since water gas producers work almost exclusively on this principle, where the maximum production of Hydrogen is sought, the independent operation of the second stage of the reaction, the replacement of Carbon monoxide by an equivalent of Hydrogen, must be provided for.

Replacement of Carbon monoxide by Hydrogen, by interaction with steam

1. *The Badische Continuous Catalytic Process.* This reaction,



can be carried out with any technical mixture containing Carbon monoxide, by mixing with a suitable excess of steam and passing over a catalyst, generally consisting of a basis of Iron oxide, with promoters, at 450–600° C, never rising above 650° C.

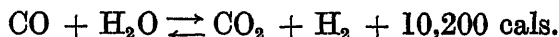
This process was first proposed by Hembert and Henry in 1884 (E.P. 1193), as follows: Steam was passed through a bed of incandescent coke, and the gaseous product obtained mixed with more steam and passed through retorts packed with a refractory material at red heat. The Carbon monoxide was replaced by an equivalent each of Carbon dioxide and Hydrogen, and the former removed by absorption in Lime. Read, shortly after (E.P. 3776 of 1885), proposed the use of catalysts, mentioning metallic oxides, and also suggested the removal of the Carbon dioxide by absorption in alkalis, or by solution in water at high pressure.

The next advance was marked by Mond and Langer's patent, E.P. 12608 of 1888. According to this process, Carbon monoxide or hydrocarbons were passed over Nickel at 350–400° C., or over Cobalt at a somewhat higher temperature, 400–450° C. In each case decomposition occurred, the Carbon monoxide into Carbon dioxide and Carbon, the hydrocarbons into Hydrogen and Carbon, the Carbon remaining in intimate union with the catalyst. On introducing steam, this Carbon readily reacted to yield low-temperature water gas, consisting of a mixture of 2 parts by volume of Hydrogen and 1 part of Carbon dioxide. This sequence of reactions was shown to occur together when mixtures of Carbon monoxide and steam, or hydrocarbon and steam, were passed over Nickel or Cobalt, the product consisting chiefly of Hydrogen and Carbon dioxide, in the proportions by volume of 1 to 2. The catalyst was prepared by impregnating Nickel chloride or Cobalt chloride in pumice, drying, and reducing in Hydrogen.

These patents describe all the features of the modern water gas processes for the manufacture of Hydrogen, but neither these nor numerous later ones were applied on a technical scale. The industrial development of the water gas–Hydrogen process was due to

the Badische Company, who eventually adopted it in connection with the Ammonia synthesis, while now, in all coal-producing countries, it has become by far the chief source of Hydrogen, yielding the gas more economically than any other known method. It is variously described as the "Badische continuous catalytic," or the "B.A.M.A.-G." process. Details of working have been given in the chapter on Ammonia, and need not here be repeated.

From the equations



$$K = \frac{[\text{H}_2][\text{CO}_2]}{[\text{CO}][\text{H}_2\text{O}]}$$

it is apparent that low temperatures are conducive to formation of Hydrogen and Carbon dioxide. The favourable condition of the equilibrium is, however, offset by the impracticable slowness of the reaction at 400° C., or lower. The variation of the equilibrium constant with temperature is shown in the table :—

| Temperature (°C.) . | 400 | 500 | 600 | 700 | 800 | 900 | 1000 |
|----------------------------------|------|------|------|------|------|------|------|
| Equilibrium Constant (K) | 0.06 | 0.16 | 0.32 | 0.58 | 0.90 | 1.25 | 1.62 |

For maximum conversion into Hydrogen and Carbon dioxide, it is therefore necessary to work at the lowest practicable temperature, and in consequence to employ a catalyst of the highest possible activity.

Increasing the concentration of steam likewise moves the equilibrium in the direction of greater conversion into Hydrogen and Carbon dioxide. This advantage of excess of steam, however, is eventually balanced by its diluting action, which lowers the reaction velocity and prolongs the time of contact necessary for the attainment of equilibrium. The effect of steam concentration on the equilibrium is shown in the following table :—

| Temp. (°C.). | Percentage of Carbon monoxide remaining in the equilibrium mixture. (Volumes of steam per volume of CO and H ₂ entering.) | | |
|--------------|--|---------|---------|
| | 3 Vols. | 4 Vols. | 5 Vols. |
| 400 | 0.45 | 0.33 | 0.26 |
| 450 | 0.80 | 0.58 | 0.46 |
| 500 | 1.25 | 0.91 | 0.71 |
| 550 | 1.80 | 1.31 | 1.03 |
| 600 | 2.45 | 1.78 | 1.40 |
| 650 | 3.20 | 2.32 | 1.83 |
| 700 | 4.05 | 2.94 | 2.24 |

At suitable working temperatures, replacement of Carbon monoxide by Hydrogen can therefore be carried almost to completion when a suitable catalyst and space velocity of the reacting gases are employed. The excess of steam produces an important but diminishing effect on the equilibrium.

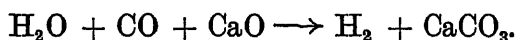
The process as developed by the Badische Company was exactly described in F.P. 375164 of 1906 of the Cie du Gaz de Lyons, who proposed to pass water gas with excess of steam over Ferric oxide at 600° C. The first Badische patent, E.P. 26770 of 1912, specified an Iron or Nickel catalyst, and claimed that the method was especially suited for the removal and utilisation of small quantities of Carbon monoxide. This could be effected even more advantageously at 4 to 40 atmospheres pressure, when, with the catalyst at 300–600° C., removal of Carbon monoxide was practically complete. The use of pressure conserved heat, rendering the process easily autothermic, but this advantage has been secured more simply in practice by efficient heat interchange and other means, and pressure is never employed. A modification of this patent, E.P. 27117 of 1912, proposed to achieve autothermic working by adding a little Oxygen to the reacting gases. It also suggested that where the proportion of Carbon monoxide was low and the amount of steam required therefore small, both the necessary energy and the steam could be advantageously supplied in this way.

The catalysts were described in E.Ps. 27955 of 1912, 8864 and 27963 of 1913, and D.R.-PP. 279582, 282849, and 284176. For the most part, these consist of Iron oxide, with various promoters, working within a temperature range of 400–500° C., avoiding a temperature above 650° C. Promoters for Iron oxide catalysts are oxides of the rare earth metals, Chromium, Thorium, Uranium, Glucinum, and Antimony, and, given a suitable contact mass, the reaction proceeds almost quantitatively at a relatively low temperature. Other catalytic metals, especially Nickel and Cobalt, are also mentioned, but these are liable to produce Methane. This tendency, it is claimed, is overcome if the catalyst contains preponderating quantities of Iron or Chromium, in addition to Nickel (preferably) or Cobalt. Spathic iron ore, with Aluminium hydroxide added as a binding agent, is protected by E.P. 16494 of 1914, and is an effective catalyst if used at a temperature below 650° C.

Among the other numerous patents that have appeared, claiming different catalysts, or applying the reaction to various technical gas mixtures, the following by Buchanan and Maxted may be mentioned: E.P. 6476 of 1914 claims "Lixivated alkaline ferrite" made by roasting burnt pyrites with Sodium carbonate at about 1000° C. and extracting the caustic Soda formed with hot water. According to E.P. 6474 of 1914, certain metallic couples, especially Iron and

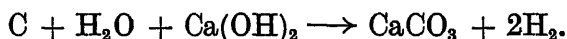
Copper or Iron and Silver, are energetic catalysts when water gas and steam are passed over them at 500° C. The Iron-Copper couple may be made in various ways, for example, from Sodium ferrate and a Copper salt, or as follows: Iron oxide is strongly heated with Sodium carbonate and the product washed to remove the caustic alkali formed. The residue is then reduced with Hydrogen and when cool moistened with a solution of Copper nitrate, and, finally, again heated in Hydrogen.

2. *The Griesheim-Elektron Process.* This method of replacing Carbon monoxide by an equivalent of Hydrogen, which we have already referred to (see also page 455), uses heated Lime or other alkalies to serve both as catalysts and as reagents for combining with the Carbon dioxide formed, this giving a pure gas, and enabling the reaction to proceed to completion (E.P. 13049 of 1912),



The elimination of Carbon monoxide is almost complete. As is well known, impregnation of Carbon with Sodium carbonate much lowers the temperature at which it is attacked by steam, but in this case the Carbon dioxide formed is not removed.

Later additions or modifications of the original patent protected the use of pressure, and also the device of producing water gas, and replacing the Carbon monoxide in it, in one step, as follows: Carbon, in the form of lignite or wood charcoal, was intimately mixed, or impregnated with alkali or alkaline-earth oxides or hydroxides, heated to a high temperature, and steam passed. Water gas production, followed by replacement of the Carbon monoxide by Hydrogen, then occurred together, the total effect being



With lime and charcoal, a temperature of 600–800° C. was necessary, when, with steam at 10 atmospheres pressure, almost pure Hydrogen was obtained (D.R.-P. 284816). Using Baryta or the alkalies, a lower temperature was stated to be practicable. A metal, or metallic oxide promoter, such as Iron or Nickel, still further facilitated the action, considerably lowering the temperature at which a mixture of Carbon and Lime was attacked by steam. According to U.S.P. 1173417, Carbon monoxide and steam (free from Nitrogen), in the proportions of 1 to 5 by volume, are brought into contact by a counter-current principle with a mass at 500–550° C., consisting of lime, CaO, containing 5 per cent. of a metallic oxide, usually Iron oxide.

When no promoter is present, the action between Lime, Carbon, and steam has been shown to occur mainly at the surface of the lime, the ordinary water gas reaction occurring to a relatively small extent.

When 5 per cent. of reduced Iron is also present, then the reaction is an ordinary contact gas reaction, and at constant temperature the presence of the Iron may augment the speed of the reaction tenfold.

The Catalytic Reduction of Carbon Monoxide

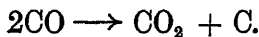
Sabatier and Senderens, in 1905, suggested the probability that, since Carbon monoxide is unsaturated, addition of Hydrogen should be possible to give, first, $\text{H}\cdot\text{C}\begin{smallmatrix} \text{O} \\ \diagup \\ \text{H} \end{smallmatrix}$, and then $\text{CH}_3\cdot\text{OH}$, just as Chlorine, Sulphur, and Oxygen can be added to give saturated products (*Ann. Chim. Phys.*, 1905, (8), 4, 418). Methane, however, was the only product which these investigators were able to obtain as the result of action between Carbon monoxide and Hydrogen in presence of a catalyst, due, as we now know, to confining their attention to the powerful hydrogenating metal catalysts.

When a mixture of Carbon monoxide and Hydrogen is passed over active Nickel, reaction commences at 180–200° C. The speed of the reaction rapidly increases as the temperature is raised, and becomes very fast at 230–250° C.,



If the proportions of Carbon monoxide and Hydrogen are correctly adjusted (25 per cent. CO, 75 per cent. H_2), almost pure Methane results from the action of catalytic Nickel at 240–250° C., the volume of the gaseous mixture diminishing to one-quarter as a result of the reaction. So long as the temperature is carefully regulated and the gases are well purified from anticatalysts, the Nickel is not altered in the reaction, and is active for an indefinite period.

At temperatures above 250° C., a secondary reaction takes place, the Carbon monoxide suffering decomposition to Carbon dioxide and Carbon, which is deposited in a very finely-divided form on the catalyst, and gradually reduces its activity,



As the temperature of the catalyst is still further raised, the subsidiary reaction becomes more marked, and unchanged Hydrogen, as well as Carbon dioxide and Methane, appear in the product. Thus, a mixture of 25 per cent. Carbon monoxide and 75 per cent. Hydrogen at 250° C. in contact with Nickel gives almost pure Methane. At 380° C., the composition of the gaseous product is:—

| | | | | | | | |
|---------------|---|---|---|---|---|---|----------------|
| CO_2 | . | . | . | . | . | . | 10.5 per cent. |
| CH_4 | . | . | . | . | . | . | 67.9 " |
| H_2 | . | . | . | . | . | . | 21.6 " |

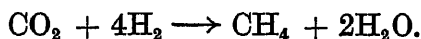
and if water gas, consisting of Carbon monoxide and Hydrogen in equal volumes, is used, the gaseous reaction product at 380° C. is :—

| | | | | | | | |
|-----------------|---|---|---|---|---|---|----------------|
| CO ₂ | . | . | . | . | . | . | 52.5 per cent. |
| CH ₄ | . | . | . | . | . | . | 39.8 ,, |
| H ₂ | . | . | . | . | . | . | 7.1 ,, |
| CO | . | . | . | . | . | . | 0.6 ,, |

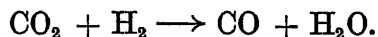
(Sabatier and Senderens, *C.R.*, 1902, 134, 514, 689).

The Catalytic Reduction of Carbon Dioxide

When Carbon dioxide and Hydrogen are passed over active Nickel, action commences at 230° C., becomes rapid at 300° C., and if excess of Hydrogen is used no complication occurs until 400° C. is reached,



If insufficient Hydrogen is used, Carbon monoxide is formed, as well as Methane,

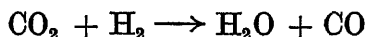


Using a small excess of Hydrogen over that indicated by theory (20 per cent. CO₂, 80 per cent. H₂), the Carbon dioxide is almost completely reduced, and at 300° C. this reaction constitutes an advantageous method of preparing Methane of a fairly high degree of purity. The purification can be completed by absorbing the small quantities of unchanged Carbon dioxide and then condensing the Methane by means of liquid air.

Other Catalysts. Cobalt can be used in place of Nickel for the reduction of either Carbon monoxide or Carbon dioxide, but it is less energetic. Reduction of Carbon monoxide commences at 270° C., but at 300° C. the decomposition to Carbon dioxide and Carbon is noticeable, and this reaction becomes more prominent if the temperature is raised or the percentage of Carbon monoxide in the gases is increased. Carbon dioxide commences to be reduced by Cobalt at 300° C., and reduction is rapid at 360–400° C. No oxidation of the metal occurs, and no deposit of Carbon is formed.

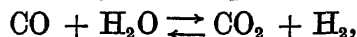
It has frequently been stated that Platinum, Palladium, and reduced Iron are unable to reduce the oxides of Carbon to Methane at the ordinary pressure. This, however, is not strictly true, since much depends upon the mode of preparation of the catalyst. They certainly are not so advantageous as Nickel for preparation of Methane, always giving a mixture of gases from which the separation of Methane is difficult. The decomposition of Carbon monoxide to Carbon and Carbon dioxide is easily effected in presence of these catalysts, while finely-divided reduced Copper at 430° C. converts a

mixture of Carbon dioxide and Hydrogen into Carbon monoxide and water,



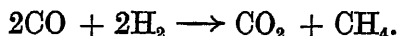
(Sabatier and Senderens, *C.R.*, 1902, 134, 689).

Fester and Brude have shown that in the reduction of Carbon monoxide by Hydrogen in presence of very active catalysts at a low temperature, for example, Palladium, mounted on activated charcoal or Silica gel supports at 35° to 240° C., appreciable amounts of Carbon dioxide are formed, as follows:—



both reactions being favoured by a low temperature (*Brenn. Chem.*, 1924, 5, 49).

The choice of catalysts for Methane formation is wider if Carbon monoxide and Hydrogen are used under pressure. Thus, Fischer and Tropsch (*Brenn. Chem.*, 1923, 4, 193) showed that when water gas at 40 atmospheres was passed over Iron filings at 400–420° C., the following reaction occurred:—



The Iron filings in time crumbled to a powder, consisting of a mixture of Iron, Iron carbide, and Carbon. Sulphur compounds completely poisoned the catalyst. The best results were obtained with water gas consisting of 40 per cent. of Carbon monoxide and 50 per cent. of Hydrogen, when the resulting gas contained 33·5 per cent. of Methane. A little Ethane was formed.

Medsforth has recently shown that the reduction of oxides of Carbon in contact with Nickel is promoted by the presence of those oxides which function as dehydrating catalysts. The most active promoters are oxides of Cerium, Thorium, Glucinum, Chromium, Aluminium, Silicon, and Zirconium, their activity following the order in which they are mentioned (*J.C.S.*, 1923, 123, 1452).

Technical Application of the Catalytic Reduction of Oxides of Carbon

A number of attempts have been made to apply these reactions technically to the production of a non-poisonous gas of high calorific value from commercial gases containing Carbon monoxide and Hydrogen, such as water gas, Riché gas, Dowson gas, Siemens gas, etc. No considerable development, however, has resulted, since the value of the gas is not sufficiently increased to make the process profitable.

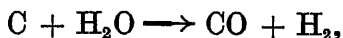
The first patents were taken out by Elworthy (E.Ps. 12461 of 1902, 14333 of 1904), who, starting with water gas, first extracted

the Carbon dioxide and then enriched with Hydrogen to produce a mixture of approximately 25 per cent. Carbon monoxide and 75 per cent. Hydrogen. Attempts were made in England to exploit the process, but were unsuccessful owing to the short life of the catalyst.

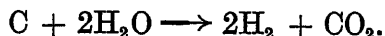
In 1905, Sabatier turned his attention to the subject, and the following patents appeared; F.Ps. 354621, 355325, 355419, 355900, 356471, all of 1905, and 400656 of 1908, also E.Ps. 14971 and 27045 of 1908. Simultaneously, the Cedford Gas Process Company in England were attempting its economic exploitation. The results obtained by the various investigators were as follows:—

Sabatier's first experiments aimed at the direct reduction of oxides of Carbon by Hydrogen in presence of Nickel at 350° C. The later patents are more important and describe the following processes (see also "La Catalyse en Chemie Organique").

1. At a high temperature, steam and Carbon react as follows:—



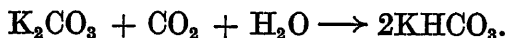
while at lower temperatures the reaction tends to become



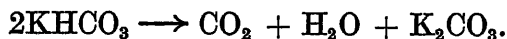
At a bright red heat, Sabatier obtained water gas of intermediate composition, indicated by the equation:



The Carbon dioxide was then removed from this mixture by either of the following methods: (a) Compressing the mixture and washing with cold water. The Carbon dioxide, being most soluble, was almost entirely removed from the compressed gases, with relatively small losses of Hydrogen and Carbon monoxide. (b) Absorbing the Carbon dioxide in strong aqueous Potassium carbonate solution.



The Potassium carbonate solution being recovered after each operation by boiling.

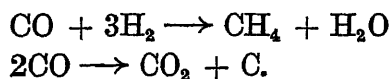


After removal of the Carbon dioxide, a gas mixture of approximately the theoretical composition, $\text{CO} + 3\text{H}_2$, remained, and was passed over finely-divided reduced Nickel at 250° C. Methane of a high degree of purity was obtained, and five volumes of water gas gave one volume of Methane.

2. Sabatier next attempted to alternate two series of reactions as follows (F.P. 355900):—

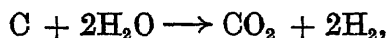
1st Phase: High-temperature water gas consisting approxim-

ately of equal volumes of Carbon monoxide and Hydrogen was passed over Nickel at 400–500° C. All the Carbon monoxide disappeared, and a mixture of Methane, Carbon dioxide, and finely-divided Carbon was obtained, the Carbon remaining intimately mixed with the Nickel,

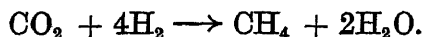


After absorbing the Carbon dioxide, a gas very rich in Methane, approximately 84 per cent. CH_4 and 15 per cent. H_2 , was obtained, of calorific value 7800 cal. per cubic metre.

2nd Phase: Superheated steam was passed over the intimate mixture of Nickel and Carbon obtained in the 1st phase, the temperature being still maintained at 400–500° C. Hydrogen and Carbon dioxide were first formed,

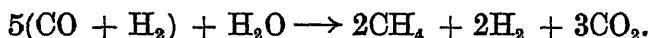


which partially interacted in presence of the Nickel with production of Methane,



The gaseous product in the second phase was therefore a mixture of Carbon dioxide, Methane, and Hydrogen, which after absorption of the Carbon dioxide gave a gas rich in Methane, and of high calorific value, though in both respects somewhat inferior to the gas produced in the 1st phase. During the 2nd phase, Carbon was eliminated from the catalyst, which was then ready for another 1st phase operation.

3. The two sets of reactions just described can be superimposed. Suitable proportions of water gas and superheated steam are passed over Nickel at 400–500° C. All the Carbon monoxide disappears, and a mixture of Carbon dioxide, Methane, and Hydrogen is obtained. The Carbon dioxide is then separated as before, and a mixture of Methane and Hydrogen, containing 45–50 per cent. of the former, produced, having a calorific value of about 5800 cal. per cubic metre,



Five volumes of water gas give therefore 2 volumes of gas rich in Methane, which is almost free from Carbon monoxide.

4. Substitutes for water gas were proposed, such as those mentioned. Riché gas, obtained in the destructive distillation of wood or cellulose, contains chiefly Carbon monoxide, Hydrogen, Methane, and Carbon dioxide.

All attempts at large-scale working have been based on one or

other of the four processes just described, the only variations consisting in different methods of preparing and purifying the original gas mixture. In transferring to the manufacturing scale, the following difficulties, not met with on the smaller scale, at once arose.

1. The theoretical proportions of Carbon monoxide and Hydrogen are 1 : 3. In practice, more Hydrogen, at least 1 : 5, was found necessary to secure complete reduction.
2. Presence of anticatalysts, especially Sulphur compounds, quickly disabled the Nickel.
3. Deposition of Carbon on the catalyst occurred when insufficient Hydrogen was used or when the temperature became too high.

The first and third difficulties disappeared together when gas sufficiently rich in Hydrogen was used. Sabatier first proposed to make such a mixture from water gas of suitable composition by absorbing the Carbon dioxide, a wasteful method. Later he proposed (F.P. 356471) to enrich high temperature water gas with Hydrogen (made from steam and Iron at 1000° C.), as first attempted by Elworthy, in the large-scale experiments already mentioned. Elimination of catalytic poisons was satisfactorily effected by passing the reaction gases over metallic Copper heated to 600° C.

According to Mayer and Henseling, Hydrogen slowly reacts with finely-divided Carbon in intimate contact with catalytic Nickel at 300° C., giving Methane. If, therefore, a Nickel catalyst loses activity owing to deposition of Carbon, the supply of Hydrogen can be increased, and the rate of passage of gases reduced until the activity is restored (*J. f. Gasbeleucht*, 1909, 52, 169, 197).

By these expedients the difficulties mentioned were overcome, but economic large-scale working was not achieved. The most successful method for obtaining a suitable gas mixture free from catalytic poisons was based on Frank and Caro's method for obtaining Hydrogen from water gas. High temperature water gas was cooled until sufficient Carbon monoxide had liquefied to leave an uncondensed gaseous residue containing rather less than 20 per cent. of Carbon monoxide. From this gaseous residue, traces of Carbon dioxide were then absorbed. By this means, the proportion of Hydrogen in the gases was raised sufficiently to ensure complete reduction of the Carbon monoxide and prevent deposition of Carbon on the catalyst, while all the anticatalytic substances were condensed with the liquid Carbon monoxide. The excess of Carbon monoxide was used as fuel to drive the compressors. When the gas mixture was made in this way, very large volumes could be treated before the activity of the Nickel became in any way impaired and the action was extremely rapid. Also, since the reaction is strongly exothermic, no external heat supply was required to maintain it.

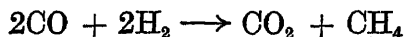
Rideal and Taylor, "Catalysis in Theory and Practice," give the following particulars. On cooling high temperature water gas to the temperature of liquid air, the uncondensed residue contained about 14 per cent. of Carbon monoxide. Some of the liquefied gas was vaporised to raise this proportion to 17 per cent. Three million volumes of this gas mixture were passed over one volume of catalyst, leaving it as active as formerly. From three quartz tubes $1\frac{1}{2}$ metres long and 12 centimetres internal diameter, and containing 200 grams of finely-divided Nickel at $280-300^{\circ}\text{C}$., 400 cubic feet of Methane rich gas per hour were prepared.

Until recently, large-scale operations have been directed towards obtaining fuel gas of high calorific value, rather than pure Methane. Sabatier proposed to confer illuminating power by adding a small percentage of Acetylene to the gas rich in Methane and passing the mixture again over catalytic Iron, Nickel, or Cobalt at $100-200^{\circ}\text{C}$. Only the Acetylene was thereby acted upon, olefines being produced which imparted great luminosity.

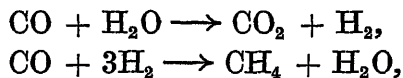
Production of Pure Methane. Fairly pure Methane, we have found, can be obtained on a small scale by the method of Sabatier and Senderens (*C.R.*, 1902, 134, 514, 689). In transferring this process to the large scale, certain difficulties were met with which were not overcome until a gas mixture containing less than 20 per cent. of Carbon monoxide was employed. From such a mixture it was impossible in one operation to obtain a product containing more than 33 per cent. of Methane, with 66 per cent. of Hydrogen. This proportion of Methane can be raised to 80-85 per cent. by repeatedly passing the gas mixture over the catalyst, adding a suitable proportion of Carbon monoxide, and removing the water formed between each passage. By this means, the 20 per cent. proportion of Carbon monoxide can be much increased without leading to carbonisation of the catalyst, and almost complete consumption of the Hydrogen can be effected (see also M.L.B., E.P. 146110 of 1919).

Various methods of preventing carbonisation of the catalyst, and so enabling approximately theoretical proportions of the reacting gases to be used, have been suggested. Meister, Lucius, und Brüning (E.P. 161924) claim an advantage for using diluted gases. Methane is proposed as a diluent, and a supply of Carbon monoxide and Hydrogen in suitable proportion maintained. Water must be removed continuously. B.A.S.F., D.R.-P. 366791 of 1921, adds small quantities of Alumina to activate the Nickel, which can then be used alone or mounted on a clay support. Carbon monoxide and Hydrogen, with little more than the theoretical proportion of the latter (1:3.4 to 3.6), when passed over this catalyst at 240°C ., give a mixture of 84 per cent. Methane, 15 per cent. Hydrogen, and 1 per cent. Carbon monoxide.

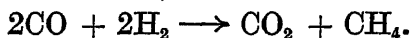
Armstrong and Hilditch (*Proc. R.S.*, 1923, 25, and E.P. 196023 of 1921) draw attention to the practical possibilities of the reaction



for the preparation of Methane. This reaction occurs in contact with certain metals, of which Nickel is the best, at temperatures between 200° C. and 300° C., but it is never complete. The reaction probably takes place in the two well-known stages,

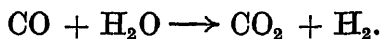


which on addition give



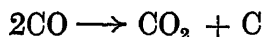
In practice, all the Carbon monoxide can be removed from water gas by repeated passage over Nickel at 240–270° C.

Meister, Lucius, und Brüning (E.P. 186899 of 1922) obtained Methane nearly free from Hydrogen by passing steam and Carbon monoxide over a Nickel catalyst. The first reaction was

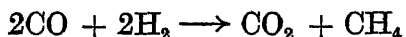


Interaction between the Carbon dioxide and Hydrogen ensued, with formation of Methane, and this reaction (reversible) was carried practically to completion by withdrawing water from the product, and passing over a second Nickel catalyst.

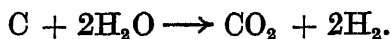
The reactions leading to formation of Methane have been investigated recently by Chakravarti and Ghosh (*J. Indian C.S.*, 1925, 2, 150; 2, 157), who used a catalyst consisting of 73 per cent. charcoal and 27 per cent. of Nickel, made by carbonising a mixture of sugar and Nickel acetate. This catalyst was found to be active for months when a mixture of 25 per cent. of Carbon monoxide and 75 per cent. of Hydrogen was passed over it, the reaction



being entirely suppressed. Some Carbon dioxide was formed, but was due mainly to the reaction



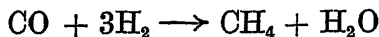
and partly to



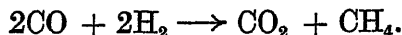
The space velocity below which no Carbon monoxide escaped reaction was large, and increased as the temperature was raised. In confirmation of Medsforth's observation, Ceria was found actively to

promote the reaction. Thus, at 355° C., in the absence of Ceria, the critical space velocity was 3.5, whilst in presence of Ceria it rose to 4.4.

In their second paper, Chakravarti and Ghosh used water gas, consisting approximately of equal volumes of Carbon monoxide and Hydrogen, and investigated the production of Methane in accordance with the reactions



and



The Nickel-charcoal catalyst was not very efficient unless a promoter was added. Ceria was not satisfactory, since it was without influence on the second reaction. Ferric oxide, or still better, Vanadium pentoxide, was very effective, and at 400° C. the temperature was easily maintained by the heat of reaction. The catalyst retained its activity for a long time.

Methane as made by either of the methods described always contains varying amounts of Nitrogen, Carbon monoxide, Hydrogen, and Carbon dioxide. After extracting the Carbon dioxide, the resulting gas may contain up to 85 per cent. of Methane, depending upon the purity of the original gases and the mode of working. Two methods are available for the further purification.

1. Selective combustion. Hydrogen and Carbon monoxide can be completely burnt without any attack on the Methane. This is best carried out by passing the gases over granular Copper oxide at 250–350° C., when only the Carbon monoxide and Hydrogen are consumed. The Copper oxide can be periodically regenerated by passage of air.

2. Liquefaction. A complete separation of Methane from Nitrogen and Hydrogen can be obtained by refrigeration, when Methane condenses much more readily than the other gases. The separation of pure Methane from natural gas, containing 75 per cent. upwards, has been accomplished by the Linde and Claude methods, and with suitable modification these are applicable to the synthetic mixture.

Syntheses from Carbon Monoxide and Hydrogen

Within recent years it has become apparent that water gas is an important potential source of pure organic chemicals (*e.g.*, Methyl alcohol), and of volatile liquid fuels. Considering first the question of fuels, the following tables indicate the quantities required by a large modern industrial community, and the manner in which they are supplied :—

Coal mined (in millions of tons).

| | Year 1913. | Year 1924. |
|-------------------------------------|------------|------------|
| United States | 509 | 512 |
| Great Britain | 287 | 267 |
| Total for other countries | 340 | 269 |

Oil produced (in millions of gallons).

| | Year 1924. |
|-------------------------------------|------------|
| United States | 24980 |
| Total for other countries | 10342 |

Oil imported into Great Britain (in millions of gallons).

| | Year 1924. |
|--------------------------------|------------|
| Crude Oil | 465.2 |
| Motor Spirit | 422.3 |
| Fuel and Burning Oil | 577.4 |
| Lubricating Oil | 101.7 |
| Total | 1566.6 |

Since natural coal and oil resources bear no relation to the varying proportions in which they are required, the production of liquid fuels from coal must be recognised as an important technical problem for all coal-producing countries which aspire to become independent of external sources. A certain proportion of liquids, up to 10 gallons of tar per ton of coal treated, is obtained in the ordinary gasworks procedure of destructive distillation. Recent methods of coal distillation depending upon the use of a lower temperature, whereby a larger proportion of the liquid products escape complete carbonisation, have shown that the amount of tar that can be obtained from 1 ton of coal may be considerably increased; up to 20–25 gallons on a laboratory (assay) scale, or considerably less, on account of mechanical difficulties, in semi-technical practice. It is plain that even if all the coal mined were to be treated in this way for the production of the maximum of liquid fuels, the proportion of liquid to solid fuels obtained would still be deficient in the former, and accessory sources, such as distillation of bitumen, peat, oil shale, fats, and waxes would still not suffice.

Research along a number of directions has been carried out with a view to correct this balance. Neglecting the fermentation processes, the following methods have been described :

Berthelot, in 1866, heated Acetylene at ordinary pressure and observed its polymerisation to Benzene and tar-like hydrocarbons.

Engler obtained an artificial petroleum by destructive distillation of fish oils, and on this result based his well-known theory of formation of natural petroleum.

Sabatier, in 1897, passed Ethylene over a Nickel catalyst at a temperature above 300°C. , and obtained a mixture of gaseous and liquid hydrocarbons, together with a coke-like solid. In 1899, the same investigator passed Acetylene and a mixture of Acetylene and Hydrogen at the ordinary pressure over various metallic catalysts, and obtained gaseous and liquid hydrocarbons of petroleum-like character, saturated or otherwise, according to the proportion of Hydrogen, and other conditions employed.

Ipatiev, in 1906, caused Ethylene to polymerise to a mixture of Hydrocarbons of average composition represented by the formula C_nH_{2n} , by heating under high pressure at $400\text{--}500^{\circ}\text{C.}$, preferably in presence of certain catalytic agents, such as anhydrous Aluminium chloride.

These methods are clearly of no technical importance, involving the use of initial materials much too costly, or inaccessible, for fuel. Only coal, or a coal product, can be seriously regarded as a starting substance, and of the methods mentioned only those using Acetylene could be founded upon coal as the basic material.

Orlov, in 1908 (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1588), observed that when Carbon monoxide is reduced by Hydrogen at a low temperature (100°C.) in presence of an active catalyst (Nickel and Palladium mounted on asbestos were used), unsaturated hydrocarbons were formed. The catalyst soon became inert. This observation has been confirmed by Fester (*Brenn. Chem.*, 1922, 3, 224), and in some respects anticipates the important recent work of Fischer and Tropsch.

In 1913, the first announcement appeared by the Badische Anilin- und Soda-Fabrik of a successful synthesis of more complex carbon compounds from water gas, depending upon contact with a catalyst at high temperature and pressure (E.P. 20488 of 1913, D.R.-P. 293787). Investigations with water gas were continued by Franz Fischer and collaborators, especially Tropsch, who, using an alkalisied iron catalyst, reduced Carbon monoxide with Hydrogen and obtained a liquid mixture termed "Synthol," which, it was proved, could replace natural petrols as a motor spirit. In their first experiments, using pressure, Fischer obtained a liquid mixture containing alcohols, aldehydes, acids, ketones, and esters, but almost free from hydrocarbons. Very recently, using a pure metal catalyst, carefully prepared, and of the very highest activity, Fischer and Tropsch have demonstrated the possibility of dispensing with pressure, and, working at a relatively low temperature ($200\text{--}300^{\circ}\text{C.}$), have obtained a mixture of liquid hydrocarbons almost free from oxygenated organic compounds.

Simultaneously with the development of Fischer's researches, the Badische Company had progressed in the direction of obtaining

pure organic substances by reduction with Hydrogen of Carbon monoxide, in contact with a specific catalyst. Using Zinc oxide or a mixture of which this substance was the principal constituent, the reduction of Carbon monoxide, instead of proceeding to the formation of a complex petroleum-like mixture, stopped at the Methyl alcohol stage, so that at a suitable temperature pure Methyl alcohol was formed in high yield, almost without any appreciable bye-reactions. In 1923, the production of Methyl alcohol by the Badische Company had reached a considerable scale. Independently, Patart had discovered the same reaction, and has since extended it to the preparation of higher alcohols.

The large-scale production of Methyl alcohol from water gas does not appreciably advance the question of a synthetic liquid fuel, since, as Fischer has pointed out, Methyl alcohol consisting of 50 per cent. of Oxygen is not a concentrated fuel, and its calorific value is low. Incidentally, when used in a motor engine it detonates, causing severe knocking: a fault that can be cured by adding some 5 per cent. of water, when a compression ratio of 6:1 can be obtained, with, however, a mileage per gallon not more than half that obtainable with petrol. These disadvantages hold to a rapidly diminishing degree for the alcohols next in series, where the proportions of Carbon and Hydrogen are much greater, so that if, as claimed by Patart, it should be possible to produce a considerable proportion of isoButyl alcohol from water gas simultaneously with Methyl alcohol, such a liquid mixture might yield a proportion of an economical liquid fuel.

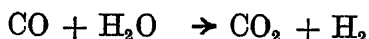
The Synthesis of Petroleum from Water Gas

It was shown by Orlov that when a mixture of Carbon monoxide and Hydrogen at the ordinary pressure was passed over an active catalyst, such as asbestos impregnated with Nickel and Palladium, at a low temperature unsaturated hydrocarbons were formed (*J. Russ. Phys. Chem. Soc.*, 1908, 40, 1588). The catalyst, however, soon became inert. Further investigations were carried out by the Badische Company, who, in the light of their experience in the synthesis of Ammonia, attempted the interaction of Carbon monoxide under pressure (D.R.-P. 293787, E.P. 20488 of 1913). A mixture of Carbon monoxide and Hydrogen, containing excess of the former, at a pressure of about 120 atmospheres, was led over various contact materials, usually metals or oxides of metals of the Iron group, impregnated with bases, such as oxides of Cerium, Chromium, Cobalt, Manganese, Molybdenum, Osmium, Palladium, Titanium, or Zinc, at a temperature of about 400° C. A liquid product was condensed, which separated into two layers, the upper oily, and the lower aqueous. The oil consisted mostly of hydro-

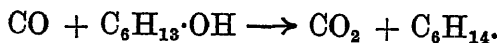
carbons, of which about 66 per cent. were stated to be saturated and 33 per cent. unsaturated, together with a smaller quantity of oxygenated bodies. Purification yielded a "petroleum" containing, in addition to hydrocarbons, alcohols, ketones, aldehydes, acids, and esters.

Synthol. Research along these lines was continued by Fischer and Tropsch, to whom the chief advances are due (*Brenn. Chem.*, 1923, 4, 276; 1924, 5, 201; Fischer, "The Conversion of Coal into Oils," English edition by Lessing, London, 1925).

In order to avoid the undesirable splitting of Carbon monoxide into Carbon and Carbon dioxide, Fischer and Tropsch used a gas mixture containing excess of Hydrogen. The catalyst employed consisted of Iron filings impregnated with strong bases. The formation of Synthol was found to occur most readily at a temperature of about 400–425° C. under high pressure, at about 150 atmospheres. The strength of the base impregnated into the Iron influenced the nature of the product, but always, in contradistinction to the results described in the Badische patents, where the condensate separated into two layers, aqueous and hydrocarbon, respectively, only an oily layer was obtained, containing very little hydrocarbon, mostly consisting of higher alcohols and ketones, with smaller quantities of aldehydes, acids, and esters. This unexpected effect of increasing the proportion of Hydrogen, reducing the proportion of hydrocarbons formed, was shown by Fischer and Tropsch to be due to a general action between Carbon monoxide and alcohols comparable with the second stage of the water gas reaction. At 400° C., in the presence of an alkalisied iron catalyst, Carbon monoxide interacts with steam, or with alcohols, as follows:—



or



Hence, as in the Badische experiments, excess of Carbon monoxide tends to convert the alcoholic into the hydrocarbon products.

Fischer and Tropsch consider that in the formation of Synthol, or hydrocarbons, from Carbon monoxide and Hydrogen, the two gases probably first combine to form Methyl alcohol, which under the conditions of the experiment undergoes further transformation. In confirmation of this, Fischer and Tropsch passed Carbon monoxide and Hydrogen over pure Zinc oxide, and obtained exclusively Methyl alcohol as the product. When, however, a second catalyst, consisting of alkalisied iron, was inserted in the circulation just following the Zinc oxide, then Synthol as before was formed. Similarly, when Methyl alcohol was heated in an autoclave to 400° C. in presence of the Iron-alkali catalyst, oily and gaseous products were formed.

Synthol, as made from Carbon monoxide and excess of Hydrogen, under 150 atmospheres, in presence of alkalised Iron at about 400° C., was found to contain the following substances:—

Alcohols: Methyl, Ethyl, Propyl, and higher alcohols up to C₉.

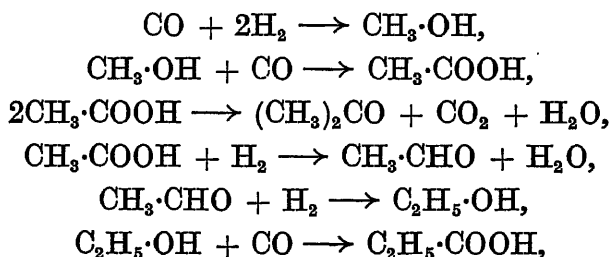
Ketones: Acetone, Methyl ethyl ketone, Diethyl ketone, Methyl propyl ketone.

Aldehydes: Acetaldehyde, Propionic, and isoButyric.

Acids: Formic, Acetic, Propionic, isoButyric, and higher fatty acids up to C₈.

Esters were formed between either of the foregoing alcohols and acids.

The strength of the base added to the Iron catalyst considerably influences the proportion in which these products are formed. A strong base conduces to oily products; a weak base to water-soluble alcoholic and ketonic products. Fischer and Tropsch suggested the following mechanism of formation of synthol:—



from which point the sequence of changes is repeated. This cycle would consume Carbon monoxide and Hydrogen in the proportions by volume of 1 to 2. Small quantities of products of greater complexity than those containing nine Carbon atoms are also formed—thus, waxy substances are present—but in rapidly diminishing quantities, since at the temperature employed, 400° C., the cracking of complex Carbon chains into simpler ones is the predominating tendency.

Synthol is a light yellow liquid which does not darken on standing. The specific gravity at 20° C. (compared with water at 4° C.) is 0.8289; its composition, Carbon 69.3 per cent., Hydrogen 12.3 per cent., Oxygen 18.3 per cent. At -30° C., solidification commences, but the oil filtered from the crystallised solid is still non-viscous. Solidification is complete at -90° C. The boiling range is as follows:—

| | | | | | | | |
|-----------------|-------|-----|-----|-----|-----|-----|-----|
| °C. | 62-80 | 100 | 120 | 140 | 160 | 180 | 200 |
| Per cent. . . . | 11 | 37 | 64 | 76 | 84 | 91 | 97 |

It was shown that, after washing free from acids, Synthol was a satisfactory motor fuel, its calorific value being 7500–8200 g. cal./gr.; as against 11,000 for ordinary petrol. A yield of synthol was obtained of about 3 kilograms per 10 cubic metres of gas mixture (composition 2 parts Hydrogen, 1 part Carbon monoxide by volume) used.

Audibert has confirmed the results described by Fischer and Tropsch (*Chem. et Ind.*, 1925, 13, 186), and given further results, using "suboxides" as catalysts. These oxides cannot be "isolated as such on account of their spontaneous oxidation to the higher state in air, e.g., CrO , V_2O , VO , MoO , UO , U_2O_3 , Pb_2O , BiO , etc.," but must be made by reduction with Hydrogen at high pressure, and in presence of a finely-divided metal to facilitate the reduction. Such catalysts, containing a suboxide as their basis, with a finely-divided metal as an accessory, have no action below 225°C . on a mixture of Carbon monoxide and Hydrogen at high pressure. Between 225°C . and an upper limit, varying according to the catalyst, but generally between 275° and 300°C ., Methyl alcohol is the main product, and often the exclusive one, while above 300°C . water, Methane, Methyl alcohol, and other more complex organic bodies resembling synthol are formed.

Synthin. When heated alone, at 400°C ., at the ordinary pressure, synthol decomposes into mainly gaseous products. In a steel autoclave, however, at 400°C ., synthol is transformed in one hour into water, gases, and a petroleum-like liquid. The petroleum layer consists half of saturated hydrocarbons, with a characteristic petroleum odour, and half unsaturated, these being extractable by solution in strong Sulphuric acid.

Fischer and Tropsch supposed that the first effect of heating under pressure was to dehydrate the oxy-bodies of the synthol to olefines, which then polymerised to Naphthenes, as shown by Ipatiev in the cases of Ethylene and Propylene. Fischer and Tropsch attach no technical importance to the transformation of synthol into synthin, its main interest consisting in the proof it affords of the possibility of obtaining Naphthenes and typical petroleums from water gas.

The Fischer–Tropsch Synthesis of Hydrocarbons at the Ordinary Pressure

More recently, Fischer and Tropsch, by careful selection and preparation of their catalyst and control of its working temperature, have suppressed almost completely the formation of Methane from Carbon monoxide and Hydrogen, and effected instead the transformation to liquid and solid products, mostly hydrocarbons, without the use of pressure (*Brenn. Chem.*, 1926, 7, 97; *Ber.*, 1926, 59, 830).

The catalysts were the metals, or their partially reduced oxides,

of Group 8 of the periodic classification, especially Iron and Cobalt, Nickel tending too easily to produce Methane, and therefore admitting less latitude and requiring more careful control in operation. Originally, promoters were added, these being selected with a view to preventing sintering, and promoting the formation of carbides, which Fischer and Tropsch regarded as formed intermediately during the reaction. Details of the preparation of catalysts have not been given, but they were made in the usual way by precipitation, or by heat decomposition of appropriate salts, followed by reduction in a current of Hydrogen at about 350°C .

A contact body consisting of Iron and Zinc oxide gave much Methane. Cobalt and Chromic oxides at 270°C . gave liquid and solid as well as gaseous hydrocarbons. One thousand litres of water gas (purified from anticatalysts), passed a number of times over the reduced oxides of Iron and Cobalt, gave 100 grams of liquid and solid hydrocarbons.

The following oxides (mentioned in the order of decreasing activity) were combined with a metal of the Iron group in proportions varying between 1:1 and 1:3, Chromic, Zinc, Beryllia, rare earths, Urania, Silica, Alumina, Magnesia, and Manganese; also active charcoal, and amorphous Carbon. The addition of weak alkalies also promoted the action, while stronger alkalies, as in the synthol process, caused higher boiling substances to be formed. Thus, a highly active contact mass consisting of reduced oxides of Iron and Copper (much more active than Iron alone) when mounted on asbestos and treated with Potassium carbonate gave from water gas much high boiling oil and solid paraffin. Sodium carbonate, instead of Potassium carbonate, led to the formation of a petroleum-like oil, while Baryta induced the formation of products of intermediate volatility.

Latterly, Fischer and Tropsch have turned to the use of pure finely-divided metals carefully prepared and free from admixture, and it is claimed that conditions are now known under which such catalysts increase in activity of themselves and retain their activity over long periods, thus saving the necessity, as formerly, of periodic regeneration.

In regard to the temperature control of the catalyst during the reaction, it is stated by Fischer that conditions conducive to Methane formation are unfavourable for the formation of other hydrocarbons from Carbon monoxide, and that it is an essential principle of the process that the reaction be carried out at temperatures below which Methane is formed rapidly, the tardiness of reaction at these temperatures ($200\text{--}300^{\circ}\text{C}$.) being compensated by superactivity of the catalyst.

Freedom from catalytic poisons, of which Sulphur in any form

is the most serious, but not the only one, is essential for the working of the catalyst, in which case any technical gas mixture containing Carbon monoxide and Hydrogen can be used. The proportions need not be equimolecular, since combinations in other proportions can occur. Purified technical water gas gave results identical with a pure synthetic gas mixture, and producer gas, blast furnace gases, and other crude mixtures can, it is claimed, be used, if purified from poisons and mixed with a suitable proportion of Hydrogen.

From 1 cubic metre of pure water gas, Fischer and Tropsch have obtained in one passage 100 grams of solid, liquid, and readily liquefiable hydrocarbons, or with a very active catalyst, a 50 per cent. yield per passage. The product formed in the reaction is removed from the unchanged gases by condensation and by absorption in active charcoal or silica gel. The unchanged gases can then be treated again, or used as fuel, or in other ways. The gaseous products, as identified, consisted of water and Carbon dioxide, Ethane, Propane, and Butane, with small amounts of Ethylene, Propylene, and Butylene. The liquid condensates were clear yellow typical petroleums, as, for example, the following: density at 20° C., 0.78 (compared with water at 4° C.). Between 170° C. and 270° C., 58.4 per cent. distilled, giving a distillate of density 0.76, and composition C 85 per cent., H 15 per cent. A further 24 per cent. distilled between 270° C. and 330° C., of density 0.79 and composition C 85.4 per cent., H 14.4 per cent. The "Benzine," of greater volatility, largely caught by adsorption in charcoal or silica gel, had a density at 15° C., 0.67, calorific value 11360 gr.cal./gr., and 96 per cent. distilled between 40° C. and 130° C. By using an Iron-Copper and a strong alkali catalyst, higher boiling products were obtained, containing a solid sparingly soluble in Acetone, from which, by repeated crystallisation it was obtained in a pure, odourless state, and identified as a higher hydrocarbon.

The formation of hydrocarbons from Carbon monoxide was tentatively explained by Fischer by supposing that high "Carbon carbides" were formed by reduction of the Carbon monoxide at the surface of the catalytic mass, these carbides being then hydrogenated to Methylene (CH_2) groups, which could polymerise, or otherwise unite, sometimes after further hydrogenation. The formation of metallic carbides with the catalysing metal would seem a more probable explanation, since catalysts are more active the greater their ease of carbide formation.

Fischer and Tropsch found no oxygenated compounds in their product, and therefore rejected the view that Formaldehyde and Methyl alcohol were intermediate products in the hydrocarbon synthesis. Elvins and Nash, while confirming Fischer in most respects, have found, however, that when a contact mass is used

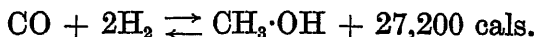
consisting of reduced Copper, Cobalt, and Manganese oxides, in addition to hydrocarbons, oxygenated compounds soluble in water are formed from Carbon monoxide and Hydrogen, these being easily isolated by absorption from the reacting gases in activated charcoal, and removal by steam distillation (*Fuel*, 1926, 5, 263; *Nature*, 1926, 118, 154; *Chem. and Ind.*, 1926, 45, 878). According to Fischer and Tropsch, however, oxygenated substances are only formed in bye-reactions, when the conditions are less favourable for hydrocarbon formation.

The relative advantages of the high and low pressure processes for liquid fuels cannot yet be assessed, but with the modern technique of high pressure processes at its present standard, it seems unlikely that low pressure methods will be the more economical, requiring bulkier and far more capacious plant, and more elaborate means for separating the volatile products.

Methyl Alcohol

The first practical suggestion of obtaining Methyl alcohol by direct synthesis from water gas was contained in the Badische patent, D.R.-P. 293787, and its British equivalent, 20488 of 1913. In 1923, large-scale manufacture was successfully inaugurated by this firm, and a large number of patents appeared. In the meantime, research in England and France had led to important results. Thus, Calvert in 1921 stated (without giving any details) that he had obtained a yield 80 per cent. of the theoretical of Methyl alcohol by passing Carbon monoxide and Hydrogen at high pressure over a catalyst (*Chem. Age*, 1921, 5, 153), and Lush, with a catalyst consisting of Nickel, Copper, and Aluminium, claimed high yields of Formaldehyde and its polymers (E.P. 180016 of 1922). Patents and publications by Patart and Audibert are of a later date, but a theoretical discussion appeared in August 1921 (Patart, F.P. 540343) considering the production of all kinds of organic compounds from Carbon monoxide, Hydrogen, Methane, or Oxygen under pressure, and a general account of the researches leading to the successful Methyl alcohol synthesis in 1924 (*C.R.*, 1924, 179, 1330). In these experiments, a mixture of Carbon monoxide and Hydrogen, in the volume proportions of 1:2, at 150 to 250 atmospheres pressure, was circulated in a closed system for 3 hours. Pure Zinc oxide, granular, or mounted upon asbestos, and heated to 400–420° C., was used as a catalyst, when, in a portion of the circuit cooled to 70° C., a liquid consisting of Methyl alcohol and a little water collected. It is to the researches and publications of Patart and Audibert, especially of the former, that the details of preparation of synthetic Methyl alcohol are so well known (Patart, *Chim. et Ind.*, 1925, 13, 179; 1926, 16, 713; Audibert, *ibid.*, 1925, 13, 186).

Theoretical. The thermochemical equation

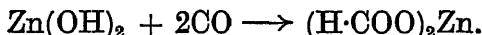


shows that the synthesis of Methyl alcohol will be favoured by increased pressure, and (consistent with a practicable rate of reaction) by diminishing temperature. The reverse change, the decomposition of Methyl and other alcohols in contact with catalysts, had been investigated by Sabatier, Senderens, Mailhe, Ipatiev, and Jahn. The last-named showed that when the vapour of Methyl alcohol was passed over heated Zinc dust, or Zinc oxide, almost the only products were 70 per cent. of Hydrogen, and 30 per cent. of Carbon monoxide, with very little Methane. Metallic Copper, made by slow reduction of the precipitated oxide, gave a similar result. Patart, therefore, supposed that these catalysts should, at a relatively high pressure, expedite the synthesis of Methyl alcohol from these gases, an anticipation realised with Zinc oxide, but not with Copper. Copper, however, is a valuable promoter for other catalysts.

Fischer has advanced another suggestion, based on the behaviour of Zinc formate when heated, to account for the Methyl alcohol synthesis. Compressed upon a heated metallic oxide, Carbon monoxide gives the formate of the metal,

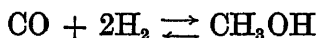


or



As shown by K. A. Hofmann, formates behave differently on heating. Whereas the formates of the alkali metals give the alkali oxalate and Hydrogen, Zinc formate gives an almost quantitative yield of a mixture of Formaldehyde, Methyl formate and Methyl alcohol. Carbon monoxide and Hydrogen under pressure, in contact with Zinc oxide, at temperatures at which Zinc formate is unstable, could therefore yield Methyl alcohol, *via* the formate. Fischer also drew attention to Goldschmidt's observation that Tin formate decomposes almost quantitatively into Formaldehyde; but the residue of Stannic oxide cannot be made to regenerate the formate by means of Carbon monoxide at any pressure, and cannot therefore behave catalytically (*J. Ind. Eng. Chem.*, June, 1925).

Various pressures, up to 200 atmospheres, have been recommended for the synthesis. The equilibria in the reaction



have not yet been experimentally determined, but it would appear that at 350–400° C. a sufficient partial pressure of Methyl alcohol can be produced to enable a certain amount of condensation to be effected even at quite low pressures (about 10 atmospheres)

of Carbon monoxide and Hydrogen. With increasing partial pressures of the reacting gases, the equilibrium is rapidly shifted in favour of Methyl alcohol formation, and at 200 atmospheres, at equilibrium, the mixture contains a considerable percentage. A high conversion is not aimed at in technical working unless the procedure consists in passing the gases at high pressure through a series of reaction chambers, condensing the product between each; the more advantageous mode consisting in a repeated circulation of the gases over the catalyst, and through a water-cooled condenser, whereby 10–15 per cent. formation and condensation of Methyl alcohol occurs at each circuit. Using a $\text{ZnO}-\text{Cr}_2\text{O}_3$ catalyst, prepared by interaction between 3 molecules of Zinc oxide and 1 molecule of Chromic acid (reduction subsequently occurs during the conditions of use), Patart passed 100 cubic metres of Carbon monoxide and Hydrogen per hour (measured at the ordinary pressure) per litre of catalyst space, obtaining 8–10 kilograms of Methyl alcohol.

The work of Patart, almost up to date, in which Methyl alcohol has been prepared on a semi-technical scale in quantities of 150 to 200 kilograms, has been described in *Chimie et Industrie*, November, 1926. The best gas mixture is the theoretical one consisting of 2 parts by volume of Hydrogen and 1 part of Carbon monoxide, pure, and free from poisons. At the same time, variations in composition are permissible so long as poisons are absent. Thus, excess of either gas, or a foreign gas, such as Nitrogen, behave merely as diluents and retard the reaction. This diluting action, it may be noted, is rapidly cumulative, since each gram-molecule of Methyl alcohol formed (32 grams) withdraws 70 litres of Carbon monoxide and Hydrogen in the correct proportions, accentuating greatly any discrepancy of composition of the original gas. Excess of Hydrogen is of less consequence than excess of Carbon monoxide, and in a high pressure circulation containing such a mixture, it is possible by protracting the reaction to combine all but a few per cent. of the Carbon monoxide. Patart claims to have used in his plant gas containing only 30 per cent. of Carbon monoxide and Hydrogen, the reaction proceeding at a rate proportional to the product of the partial pressures.

The most serious poison for the reaction is Sulphur, but, contrary to the original statements, the catalyst is not very sensitive to small quantities. To avoid parasitic reactions, especially the formation of Methane, metals of the Iron group should be avoided both in the catalytic mass and in the construction of the furnace. This must be internally lined with Copper, Silver, or Aluminium, and all heated parts of the circuit similarly constructed of some metal which cannot form a volatile carbonyl with Carbon monoxide at any pressure. Copper is preferable, but alloy steels which do not form Iron carbonyl

can be used. The presence of alkalis or alkaline carbonates in the catalyst also must be avoided, since these increase the proportion of complex products formed. The presence of soluble metallic salts also in general reduces the porosity and activity of Zinc oxide catalysts, so that a catalyst prepared by precipitation requires thorough washing, preferably with distilled water.

Catalysts. Catalysts for this reaction consist mainly of oxides, which, like Zinc oxide, are not reduced to the metal by Hydrogen under the conditions of working. A sub-oxide may be formed (Audibert), though proof of this is in many cases lacking. If the oxide forms a carbonate, this must be decomposed below 400° C., so that a fairly strong base is necessary, which cannot be permanently changed.

The original Badische patents, from 1923 to 1925, specified a large number of catalysts, promoters, and supports, mainly "mixtures of the non-reducible metallic oxides of groups 2 to 7 of the periodic table, the more basic oxide predominating in the mixture," for example, a mixture of 2 to 12, or even more, molecular equivalents of Zinc oxide to 1 of Chromic oxide. The activity of a basic oxide is generally improved by the addition of an acidic oxide, even 1 per cent. of Chromic oxide in the above example exercising a considerable influence.

Finely-divided metals, intimately mixed with a non-reducible oxide, such as an oxide of Titanium, Vanadium, Chromium, Manganese, "or other metal of the 4th to the 7th group," may also be used as catalysts. Thus, Copper further promotes the activity of the Zinc oxide-Chromic oxide catalyst already mentioned; while, as Audibert has shown, a finely-divided metal and an oxide, under the conditions of working, in general give a suboxide, which exerts some catalytic effect, sometimes very efficiently (D.R.-PP. 415469, 430623, 571354, 571355, 571356, 581816, 585169, 605349; F.P. 571285; U.S.Ps. 1558559, 1562480; E.Ps. 237030, 244830, 247217).

Various fused catalysts are described in D.R.-P. 415469, and in the basic American patent, 1558559 (1923). The English patent, 229715 (1923), specifies "one of the hydrogenating elements, Copper, Silver, Gold, Zinc, Cadmium, or Lead, associated with an oxide of either Titanium, Vanadium, Chromium, Manganese, Zirconium, Cerium, Thorium, Columbium, Tantalum, Molybdenum, Tungsten, Uranium, or Boron." Freedom from compounds of the alkali metals, Iron, Cobalt, and Nickel is essential. Carriers also may be used but these too must be free from alkalis or iron.

Audibert has prepared a number of suboxides and mixtures of suboxides with metals, which he claims to be highly efficient catalysts in the Methyl alcohol synthesis. He even postulates the prior formation of a suboxide of Zinc when Zinc oxide is employed, and

raises the analogy with hydrogenating metal catalysts, all of which have been shown to be more effective when a certain amount of unreduced oxide remains. Since the suboxides are easily reoxidised in air, they are reduced by Hydrogen in the catalytic reaction chamber just prior to use. Often, however, Hydrogen alone is unable to reduce the oxide to suboxide at a temperature below which the catalytic properties of the resulting product are destroyed. In such cases, the reduction is facilitated by the addition of a finely-divided metal, or an oxide of such a metal, in presence of which the reduction is possible at a much lower temperature. The promoting metal chosen for this purpose must be one that does not induce any parasitic reaction, the only suitable ones being Copper, which does not promote any deleterious action at all, and Nickel, which can be eliminated as Nickel carbonyl from the prepared catalytic mass in a current of Carbon monoxide at 60–80° C. In the presence of finely-divided reduced Copper or Nickel, suboxides of various plurivalent metals were prepared by Audibert, *e.g.*, Chromium, Uranium, Titanium, etc., by reduction in Hydrogen under 200 atmospheres pressure at temperatures of about 200° C. Patart and others have been unable to confirm the high efficiency claimed by Audibert using these catalysts.

Similar catalysts to those proposed by Audibert, namely, a mixture of a difficultly reducible metallic oxide (Zinc, Cadmium, Magnesium, Chromium, Vanadium, Tungsten, Uranium, Zirconium, Titanium, Aluminium, Manganese, Molybdenum, Thorium, Cerium, etc.) with an easily reducible metallic oxide (Copper, Silver, Iron, Nickel, Cobalt, etc.) have been proposed in U.S.Ps. 1625924 to 1625929 of 1927. Here the addition also of a metallic halide (Zinc chloride, Cuprous chloride, Magnesium chloride, or fluoride, Zinc bromide, Vanadium chloride, Chromium chloride, etc.) is recommended as further promoting the action of the catalyst, and enabling it to be bound into hard granules.

Recently it has appeared that Iron, Nickel, or Cobalt, or compounds of these metals, may not have so deleterious an action as was at first supposed; and the inclusion of these metals has in some cases been recommended. Thus in E.P. 254760 of 1926 some of the examples quoted employ a catalyst containing not only compounds of these metals, but also Potassium carbonate, to which is added Arsenic pentoxide to combine with any free Iron that may be formed.

The numerous patents and other information published show that many catalysts give Methyl alcohol from Carbon monoxide and Hydrogen. Only Zinc oxide, however, has attained technical or semi-technical importance, this, when prepared by precipitation from a dilute solution of a Zinc salt by adding to a dilute solution of Ammonia or Sodium carbonate, washing, and drying, commencing

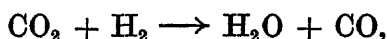
to induce reaction at about 350° C. The rate of reaction increases with increasing temperature, and proceeds almost without by-reactions up to 400–420° C. The addition of Chromic acid or other acid oxides much augments the activity—but whereas most acid oxides also increase the proportion of reduction to Methane, this deleterious influence is not exerted by Chromic acid. The yield of Methyl alcohol, under good conditions of gas concentration, and temperature, using a Zinc oxide, or a Zinc oxide and chromate catalyst, is therefore almost quantitative, less than 1 per cent. of Methane being formed, no aldehydes or ketones, and a trace only of acids, while if poisons are excluded the catalyst retains its light colour, and is active indefinitely. The percentage of Chromic acid, which forms Zinc chromate with the Zinc oxide and reduces to the lower state of oxidation (perhaps "Zinc chromite") under conditions of working, does not greatly matter. Patart recommends basic Zinc chromates of definite chemical character, especially the pigment Zinc yellow (F.P. 599588, and the corresponding E.P. 252361 of 1925, F.Ps. 540543, 593648, 593649, 598447; E.Ps. 227853, 247178, 247177; *Bull. Société d'Encouragement*, Feb., 1925, "Comité Scientifique du Pétrole," March 3rd, 1925).

As the temperature is raised above 400° C.; the formation of Methane increases, and at the same time other reactions occur, leading to the formation of higher alcohols, aldehydes, ketones, and acids. Recent work by Patart is aiming at the economic production of higher alcohols. By varying the catalyst, the proportion of these can be increased, and a yield of 10–12 per cent. of isoButyl alcohol has been obtained. No specific catalyst for either of the higher alcohols has, however, been found. Methyl alcohol itself can be converted catalytically into a complex mixture of higher products, among which isoButyl alcohol preponderates.

The suboxide-metal catalysts employed by Audibert are active at lower temperatures than Zinc chromate, the optimum point depending upon the particular mixture. Below 225° C., no action occurs: between 225° C. and 300° C. reaction takes place with formation of Methyl alcohol. Audibert claims that within the correct range of temperature this is the only reaction, but that at high temperatures secondary reactions supervene, with formation of Methane and more complex liquid products. Alkali, or alkali carbonate with a suboxide catalyst, still leads to the formation exclusively of liquid products if the catalyst temperature is below 300° C., but it is not pure Methyl alcohol, but a complex mixture of water-soluble and oily products resembling synthol (*Chim. et Ind.*, 1925, 13, 186). According to Patart and others, suboxide catalysts do not give even approximately the results claimed by Audibert ("Comité Scientifique du Pétrole," May 3rd, 1925).

The product as condensed, using the catalyst and conditions recommended by Patart, is of a high degree of purity, containing only traces of acids, water, and inorganic substances dissolved or eroded from the metal (usually Copper) of the furnace-lining and condenser. A single distillation yields a pure product, as shown by its constancy of boiling point, and the melting point of solid esters (e.g., para-Nitro benzoic).

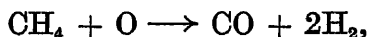
Other products in the Methyl alcohol synthesis. The presence of Carbon dioxide in the gas mixture for preparation of Methyl alcohol is quite unobjectionable; in fact, this oxide also is said to yield Methyl alcohol, being first reduced to Carbon monoxide in contact with a Zinc chromate catalyst,



which then reacts as before.

In a recent patent, Patart has suggested that a partial replacement of Hydrogen by Ethylene in the Methyl alcohol reaction would possibly result in the formation of Acetone (E.P. 247178 of 1926, F.P. 593648 of 1925). This, however, has not been realised, the Hydrogen and Carbon monoxide giving Methyl alcohol, and the Ethylene independently polymerising to the petroleum-like liquid first obtained by Ipatiev.

The formation of higher alcohols has been described in E.Ps. 247176 and 247177 of 1926 and the corresponding F.P. 593649 of 1925, the gas mixture being obtained by partial combustion of Methane,



and this (either alone or admixed with Methyl alcohol vapour), converted into liquid products of the desired boiling point by contact at high pressure with a catalyst consisting of Zinc oxide, Copper, and Potash at a high temperature. The formation of higher alcohols from water gas is also described in F.P. 598447 of 1925, the catalyst being specially prepared and containing much alkali.

These patents have aimed at the production of higher alcohols in a pure state. The following have described methods of obtaining mixtures of Methyl alcohol and other utilisable substances. According to F.P. 581816 and the corresponding E.P. 238319 of 1924 (B.A.S.F.), oily products are formed besides Methyl alcohol when the catalyst contains a considerable proportion of Potash, is used at high temperature (above 450° C.), and the gases are passed at a low space velocity. The transformation of these oils (mostly higher alcohols) into products of dehydrogenation is described in E.P. 244830 of 1924.

The Badische U.S.P. 1562480 and the corresponding F.P. 597328 protect the formation of higher products, alcohols, aldehydes, and acids by combining oxides of Carbon and Hydrogen, or Methyl alcohol and Carbon monoxide in contact with catalytic mixtures, one constituent of which is a hydrogenating metal (Cu, Ag, Au, Sn, Pb, Sb, Bi, Zn, Cd, Tl), and the other a hydrating oxide (such as oxides of Ti, Zr, Th, V, Ni, Mn, Ce, La, Ta, Cr, Mo, W, U, Di, Gl, or Al). The addition of alkali or alkaline-earth compounds to the catalyst, or of Ammonia to the reacting gases, use of a high temperature, and a slow rate of passage, are factors tending to increase the formation of high boiling oils. (See also E.Ps. 227147, 228959, 229714, 229715 of 1923 (B.A.S.F.); Schmidt and Ufer, Canadian P. 251486 of 1925; Pier, Muller, Wietzel, and Winkler, Canadian P. 251485 of 1925; Mittasch, Winkler, and Pier, Canadian P. 251484 of 1925; Pier and Muller, Canadian P. 241483 of 1925.)

The Bergius Process

The Ipatiev method of hydrogenation, in the hands of Bergius, has been developed into a means of obtaining liquid fuels directly from coal and other naturally occurring organic bodies.

Destructive distillation of coal by low temperature carbonisation gives a maximum of 16 to 20 gallons of tar per ton of coal treated. When this process is carried out in the presence of Hydrogen at high pressure and a hydrogenating catalyst, the products of the decomposition are much modified by the simultaneous occurrence of hydrogenation and carbonisation. Decomposition of bituminous coal commences below 420°C ., the lowest point at which coal is converted by hydrogenation into a product completely liquid at the ordinary temperature. Hence, under the conditions necessary for the formation of volatile liquids, carbonisation also proceeds, with the result that coke is formed, and the conversion of coal into liquid products cannot be complete.

Hydrogenation of coal commences at $300\text{--}350^{\circ}\text{C}$., in presence of Iron as catalyst, at this temperature giving a pitch, solid at the ordinary temperature, but more easily fusible than the original coal. Above 300°C ., within a considerable range of temperature and pressures of Hydrogen, the speed of Hydrogenation is greater than the speed of carbonisation. At high temperatures, the latter becomes the faster reaction, and at still higher temperatures, or with prolonged treatment, coke instead of oil is the sole product, even at very high Hydrogen pressures.

For production of volatile liquid fuels, it is necessary to hydrogenate at a temperature at which the pitch consisting of a complex mixture of organic bodies of high molecular weight, formed by direct addition of Hydrogen at $300\text{--}350^{\circ}\text{C}$., undergoes further

changes, degradative as well as hydrogenating. Above 400°C ., this mixture of complex substances is "cracked" into simpler ones, mainly liquids, taking up more Hydrogen at the same time, and forming also coke and gaseous hydrocarbons. The higher the temperature the more complete the degradation, and the lower boiling the liquid products produced. At 420°C . and 200 atmospheres of Hydrogen, the high melting pitch obtained at lower temperatures is hydrogenated and cracked, so that, depending upon the kind of coal used, from 40 to 70 per cent. of its weight of oil is obtained, which remains liquid at considerably lower temperatures than the ordinary.

In the original patents it was proposed to heat coal in a steel autoclave to a suitable reaction temperature, under high pressure of Hydrogen (20 to 200 atmospheres), when yields of oil up to 85 per cent. of the weight of coal used were claimed (Bergius and Billwiller, U.S.P. 1251954, E.P. 18232 of 1914; Bergius, U.S.P. 1342790, E.Ps. 5021 of 1915, 148436 of 1920; D.R.-PP. 303272, 303332, 307671).

Recently these experiments have been developed on a semi-technical scale, in a way to render the process continuous. The reaction vessels are steel bombs, of about 5 to 6 feet long and 4 inches internal and 12 inches external diameter. Even with such a thickness of metal, the life of a bomb is short, on account of decarbonisation by high pressure Hydrogen and other changes, which take place at the high temperature of the operation. To each Bergius set, three such bombs are arranged in series, resting on their side, and heat is applied to them by means of lead baths, carefully disposed around them in such a way as to secure even heating and afford maximum protection. The temperature and pressure in each bomb are registered by a pyrometer and a pressure gauge, and a stirrer, inserted through a special gland made tight with heat-resisting material, maintains the contents of each bomb in movement and effects the necessary contact between the liquids and Hydrogen. The best temperature for the hydrogenation is stated to be about 490°C ., use of lower temperatures necessitating a considerably longer treatment, while any higher temperature much increases the rate at which the steel bombs lose their strength. The reacting substances are delivered into the first bomb, the Hydrogen from a compressor, usually at about 200 atmospheres, and the coal, introduced at the bottom, by means of a hydraulic press. To bring the coal to a suitable form, it is powdered in a mill, and mixed with oil in an incorporator to form a paste ("Lux-masse") sufficiently fluid to be pressed through pipes. A paste, just fluid enough to pump, can be made by incorporating 1 part of oil with 2 to $2\frac{1}{2}$ parts by weight of coal dust. The oil used for this

purpose may be coal tar, a high boiling oil, or a bye-product of the process itself. A certain proportion of catalyst, usually Iron oxide, also is added to the paste. The paste, and Hydrogen, are continuously admitted into the first bomb, when hydrogenation commences, resulting in an increase of volume. The contents of the first bomb, more fluid as a result of hydrogenation, are maintained at a constant level by passing through a duct into the second bomb, similar in all respects to the first. From here, the still more fluid product is pressed into the third bomb, where hydrogenation is carried to the desired degree: the completeness of the hydrogenation and degradation depending upon the rate of passage, the temperature, and other factors. Without stirring, the reaction does not proceed satisfactorily, and the egress pipes are placed at such a level that each bomb is about half full of liquid.

From the third bomb, the liquid product and exhaust gases, still at high pressure, pass through a series of water-cooled coils to reducing valves, which lower the pressure to about 60 atmospheres, and thence to a receiver. Here the liquid product is separated from the exhaust gases, and released through a suitable valve into other vessels at atmospheric pressure. A considerable volume of gas, mostly hydrocarbons, which remained in solution in the liquid product while at high pressure, is evolved in this final pressure reduction, and is led to a gasholder for use as a fuel gas of high calorific value.

The exhaust gas, at 60 atmospheres pressure, separated from the liquid product, is conducted *via* a cooler to a tower, in which, still at 60 atmospheres pressure, it is scrubbed with oil to remove gaseous and liquid hydrocarbons. These are partially given up by the oil on releasing the pressure and used as fuel, while the scrubbed gas, consisting mostly of Hydrogen, is returned to the process.

Some 35,000 cubic feet of Hydrogen are used per ton of coal, or about 10 per cent. by weight. In a semi-technical operation, only about half of this enters into combination with the coal to form liquid products, the remainder escaping as residual Hydrogen, or in combination as gaseous hydrocarbons. The recovery of the free and combined Hydrogen, in a form sufficiently pure to use again, would be a necessary adjunct to the large-scale working of the process.

The treatment of the hydrogenated product for separation, according to their boiling points, of the different grades of liquid fuels is understood to involve considerable difficulties. Distillation is accompanied by very copious frothing, and a prior separation of the finely-divided solids, which are responsible for this, is not easy. The yield of liquid products varies between 40 and 70 per cent. by weight, or between 107 and 185 gallons of oil per short ton of crude

coal, according to the kind of coal used. From an average bituminous coal the following proportions of products have been obtained :—

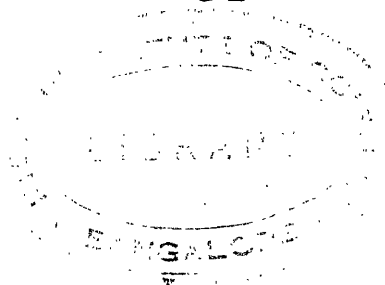
| | | | | | |
|-----------------|---|---|---|---|--------------|
| Motor spirit | . | . | . | . | 15 per cent. |
| Middle oil | . | . | . | . | 20 " |
| Lubricating oil | . | . | . | . | 6 " |
| Fuel oil | . | . | . | . | 8 " |

Half the Nitrogen of the coal is obtained as Ammonia (Bergius, Pittsburg Conference, *Min. J.*, 1926, p. 1013; King, *J. Soc. Chem. Ind.*, 1927, 184T). The higher-boiling products can be returned to the process, being used in pasting the coal dust to form the "Lux-masse."

At present there seems some doubt whether the oils obtained by simple distillation of the Bergius product can always be used for their various purposes without further treatment. A proportion of unsaturated oils are said generally to be present, but this proportion, and the other properties of the product, can doubtless be much modified by the conditions of the hydrogenation and the kind of coal used. Ormandy has examined the lighter fractions obtained from a certain coal, and found that they contain 7.5 per cent. of aromatic compounds, 37 per cent. of paraffin, and 27 per cent. of Naphthenic hydrocarbons (*J. Inst. Pet. Tech.*, 1926, 12, 77). Bergius and other workers have, however, given much higher percentages of aromatic bodies. Heyn and Dunkel obtained 44.3 per cent. of oil from a Silesian coal dust, and of this, 75.7 per cent. was a neutral oil, 12 per cent. phenolic (Phenol, the Cresols, and Xylenols were recognised), and 3 per cent. basic (Aniline, the Toluidines, Xylidines, Collidine, Quinoline, and Quinaldine. Pyridine was absent) (*Brenn. Chem.*, 1927, 7, 20, 81, 245).

The Bergius process has now reached an advanced experimental stage in which the difficulties inherent in a high temperature-high pressure process are being gradually overcome. Bergius has also claimed that his process is an advantageous alternative to "cracking" in the case of heavy oils, giving a much higher yield of light oils, less gaseous products, and no coke (*Z. angew. Chem.*, 1921, 34, 341; E.P. 192850 of 1921).

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